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CELLULOSE AND CELLULOSE DERIVATIVES

A MONOGRAPH

Prepared by a Staff of Specialists
under the Editorship of

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EMIL OTT

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Wilmington, Delaware

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PREFACE

The presentation of a book on cellulose and cellulose derivatives at this time seems particularly appropriate. The knowledge of this field of chemistry, which for years was on an entirely empirical basis, has reached the point where a number of important concepts have been formulated and substantiated in a manner which permits a simplified review of the whole field. This, of course, does not mean that the subject matter is simple. On the contrary, it is admittedly still very complex, but this complexity can now be recognized as an inherent characteristic of the field rather than as an irritating and confusing complication. Because of world conditions, the international exchange of basic scientific information will be limited, and, hence, the present over-all picture of cellulose chemistry must prevail for a number of years. The requirements of war necessitate the increased interest of many technical people in all high-polymer fields, especially that of cellulose and cellulose derivatives, and an adequate treatment of this subject matter should be of considerable help to the war effort.

In organizing this book, the primary objective has been to furnish, in a straightforward manner, digested information which is directly related to the most generally accepted present-day picture of the field. The historical approach has been almost entirely neglected, although the editor is not unaware of the pedagogic value of the customary procedure. Considerable technical detail has been omitted, and only that material was used which was deemed necessary for a broad but reasonably thorough understanding of the whole field. Then, too, the most recent references giving a good description of a point involved have been preferred over the earlier references. Not much emphasis has been placed on giving credit for ideas, as a discussion of priority is considered outside the purpose of this treatise. Nonetheless, it is felt that the bibliography is quite complete in the sense that few topics are discussed without sufficient references being given to permit locating of pertinent literature with a minimum of trouble.

To make available for the workers of today a modern, complete presentation of results secured in the immediate past, it was inevitable from the start that the contributions of many individuals would be needed. It would seem almost impossible for any one individual, and certainly the

editor would not feel qualified, to give an objective and proportionat digest of the whole field with reasonable perfection and in reasonable time The advantages and disadvantages of a collaborative volume are well known and need not be summarized.

The objective of presenting world-wide authoritative opinion in this boo might have been better attained by selecting authors from differen countries. The complications of threatened and actual war, however, an the interruptions in communications confined the selection to those residin in the United States. While it is true that most of the fundamental ad vances in cellulose chemistry originated in Europe, it is gratifying to not that a treatise of the high quality which this one represents (it is hoped tha this statement is made with reasonable objectivity) has been possible unde existing circumstances. This might be expected, as the high-polyme chemists of this country should have been able to develop a more objectiv point of view than could the originators of any particular theories. Ou debt to the European experts is acknowledged, however, for they have ad vanced many important ideas in this field and have trained many of th investigators working in this country. The uniform excellence of the vari ous contributions to this book only serves to emphasize the increasing im portance of cellulose research in the United States as compared to the res of the world.

The selection of a suitable list of authors was rendered more difficult be cause there were usually several men who were well qualified to write on a given topic. The invitation to contribute was finally given to those who it was felt, would be thoroughly interested in the task and who would b able to contribute with a minimum of delay. The response was very grati fying. In most cases, the first person who was approached accepted; th few who declined were forced to do so by other commitments. The genera interest in the project among cellulose chemists indicates that those wh are not contributors are sympathetic with the objectives of this book.

About four-fifths of the material presented in this book has been con tributed by persons engaged in industry or working in institutions supporte by industry or in government laboratories. The advantage of this is obviously, that the writers are in close contact with modern industria processes and are thus best qualified to make certain that no commercially important factors would be overlooked and that no mistaken conclusion would be drawn from the mass of ill-defined data available in the literature That such cooperation between representatives of competing industries i this field of science has been possible is convincing proof of the advance spirit in industrial research today. The contributions of the academi

authors are especially valuable because of their fundamental nature, and will be of great utility to those in industry. It is hoped that this book may stimulate further fundamental cellulose research among academic scientists.

The editor wishes to express his sincere thanks to the many authors. It has been an agreeable experience to note the unanimity of opinion of contributors on many points upon which there has been much controversy in the past. All cooperated splendidly both in regard to their own contributions and other contributions on closely related material. Their primary interest seemed to be the worth-while task to be accomplished, and they devoted much effort to it, despite the heavy burden of essential work placed on them by the entrance of the United States into the war. No one could have had a finer group of contributors with which to work both from the scientific and human standpoint, and this experience alone is adequate reward for the editorial efforts.

Since the use of many authors is apt to interfere with the continuity and other over-all aspects of a book, the editor had to make use of the prerogatives implied in the word "editor." In addition to assuming the responsibility for the selection of the authors, it was necessary to examine all of the material submitted, to discuss many points in detail with the contributors, to transpose some subject matter from one section to another, and to eliminate many duplications. In certain instances, the discussion of a particular point has been repeated at several places in order to secure clarity of presentation. In others, emphasis has been placed on abnormalities of behavior or on poorly understood phenomena subject to different interpretations. Compromises had to be reached between perfecting a certain section of the book, through lengthy exchange of ideas, and issuing the whole work as early as possible. It is obvious that, even if the editor were qualified to do all this, his other duties would prevent him from taking the necessary time. The editor has, therefore, had to rely on the capable coworkers, from the Hercules Powder Company, listed below.

Throughout the entire project, Dr. Harold M. Spurlin gave freely of his comprehensive experience in the cellulose field and of his wide knowledge of the literature. He served as technical adviser, discussed numerous points with many of the authors and contributed much to the clarification of controversial points, aided considerably in the rearrangement of specific manuscripts, and made numerous suggestions which have contributed substantially to the technical accuracy and high quality of the book.

The assistance of Miss Mildred W. Grafflin has been of invaluable help. Her editorial and printing experience in the chemical field, as well as her training on *Chemical Abstracts*, made her unusually qualified for the many

ramifications involved in the editing of a volume of this nature. It must be confessed that there have been times when the preparation of this book was not all pleasure, but her interest and her enthusiasm never lagged.

Dr. Arthur F. Martin helped with many of the manuscripts and with more than half of the proofreading. He checked much of the original literature and rewrote portions of manuscripts necessitated by one reason or another. Dr. Howard G. Tennent helped on the other half of proofreading. He and also Dr. J. K. Moore gave invaluable suggestions on the physical chemistry and mathematical sections of the book.

Dr. J. Barsha, together with Miss Grafflin, compiled the subject index. Miss Blanche Williams compiled the author index. Mrs. Virginia Clarke Stowe is responsible for the accuracy of the form of the numerous footnote references.

A great number of the illustrations and graphs for the book owe their excellence to the painstaking work of Mr. S. V. Spoor, Mr. E. G. Weatherlow, and Mr. J. S. Biddle.

It is a pleasant duty and privilege to express sincere thanks to these coworkers. Thanks are also due to the management of the Hercules Powder Company for their farsighted interest in this project.

Furthermore, acknowledgment is due to Dr. E. S. Proskauer of Interscience Publishers, Inc., and to the Mack Printing Company for their understanding cooperation.

Wilmington, Del. EMIL OTT
June, 1943

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INTRODUCTION

EMIL OTT

The object of this book is to have in a unified presentation the most important modern scientific and technical information concerning cellulose and its derivatives and to have this information in such form that it becomes a thorough introduction for work on any cellulose problem by any person with reasonably wide general technical training. To fulfill this comprehensive objective, it has been necessary to treat a wide variety of topics. These may be divided roughly as follows: structure and chemistry of cellulose and its derivatives; occurrence, isolation, and purification of cellulose; a sufficient amount of the chemistry of substances commonly occurring with cellulose to make the technical isolation processes understandable; fiber structure and its implications in respect to chemical reactions and physical uses; and physical properties of cellulose and its derivatives.

An attempt has been made to organize the book so that it can be read through from beginning to end without encountering material which presupposes for its understanding a knowledge of a topic discussed in a later section. For reasons of unity of presentation it has not been possible to attain this objective in all cases; for example, solubility and swelling behavior are treated in numerous places in connection with some of the underlying factors influencing them. An attempt has been made in the index to include satisfactory cross references for such topics.

The subject "Occurrence of Cellulose" logically comes first. There are two reasons why it was felt wise to have a separate treatment of this topic rather than to rely on incidental observations in other sections of the book. The chief one is the enormous importance of cellulose as a building material in the cell walls of plants in addition to its technical uses in the isolated state. The other reason is that the industrially important sources of cellulose are very limited in number, and a mention of these alone would not present a true picture of the widespread occurrence of cellulose in nature.

In Chapter II are laid down the fundamental properties of cellulose, its

structure, and its reactions. It is the opinion of the editor that the picture of cellulose as a system of long chains of anhydroglucose units is the most important concept in the book. From it may be derived, by the application of ordinary chemical principles, an explanation for almost all the physical and chemical properties of the molecule. A thorough understanding of the section on "Chain Structure" is a prerequisite for an understanding of all that which follows.

The division of Chapter II into sections has been designed to give due prominence to some of the relatively short topics, such as end groups and the question of combination of cellulose with lignin or hemicelluloses. These topics are very important for a complete understanding of cellulose chemistry and might be overlooked if submerged in the general treatment or referred to only in later chapters. Cellulose tests (Chapter II, Section H) have been assigned a relatively minor portion of the book because it is felt that this subject is in a quite unsatisfactory state. Most of the tests in common use originated in the days before cellulose chemistry was well understood and have only empirical significance. They do not correlate well with the usefulness of cellulose in various industries, and have been largely supplanted by use tests, based on actual applications. This criticism does not apply to viscosity, which is now on a firmer footing than ever as a criterion of cellulose properties and is accorded separate treatment in Chapter IX in addition to the discussion in Chapter II.

It has not been possible at this time to give a complete treatment to the subject of "Structure and Properties of Cellulose Fibers" (Chapter III), primarily because of the very important results to be anticipated from the application of electron microscopy to this field. Results so far obtained (Section C, 2) have furnished interesting information which indicates that the fibril is the characteristic unit of all fibers. Only a beginning has been made, but it seems likely that with this new tool the nature of the forces holding fibrils together and the distribution of amorphous material between and inside the fibrils may be studied better than ever before.

In Chapters IV ("Carbohydrates Normally Associated with Cellulose in Nature") and V ("Lignin and Other Noncarbohydrates"), the chemistry of the substances occurring with cellulose is treated. At first sight, these topics may seem somewhat foreign to cellulose chemistry. However, experience has shown that the average worker in this field does not have the opportunity to survey the literature of the hemicelluloses and lignin. These two chapters are a necessary preliminary to Chapters VI and VII for those who may wish to depend on this book for their cellulose background.

It has been considered very important to combine in this book pertinent information on the preparation (Chapter VI) and purification (Chapter VII) of cellulose, as well as on the chemistry of purified cellulose and on the utilization of cellulose in derivatives. One aspect is as important as any other, yet few workers have been familiar with all. It is particularly unfortunate that space was not available for an even more complete discussion of preparation and purification. The present scope should, however, be broad enough to satisfy the needs of those working on the utilization of cellulose, whether in the textile, paper, regenerated cellulose, or cellulose-derivative fields. Of course, those working directly on preparation and purification will wish to make use of the more complete texts on these subjects.

From the viewpoint of the industrial chemist, a very important section of the book is Chapter VIII on "Derivatives of Cellulose." With the present emphasis on plastics, particularly as replacements for rubber and metals, every effort is being made in industry to fabricate the abundant cellulose into materials of useful physical properties. The description of known cellulose derivatives should aid in predicting the results of new chemical treatments.

Of necessity in Chapter IX ("Physical Properties of Cellulose and Its Derivatives") a more speculative outlook has been adopted than in the rest of the book, for in no other portion of the cellulose field is it so necessary to revise out-of-date concepts in the light of the newest theoretical advances. This does not mean that still more satisfactory and more complete treatments of individual points will not become available. It is indeed reasonable to hope that this chapter will serve as an incentive for those who wish to refine and revise the treatment given.

It seems logical to close the book with a summary of technical applications (Chapter X). This should serve to orient the reader in the particular fields of application of cellulose and its derivatives. It is becoming increasingly clear that polymers having the characteristics required for a specific use must be built to order; it is equally clear that cellulose and its derivatives can be modified within wide limits to play an important role in any future high-polymer developments.

To summarize, this book attempts to follow cellulose from its vegetable sources through the laboratory research, which has determined its properties, into the industrial problems such as isolation and purification, derivative formation, and technical applications. Until about fifteen years ago, progress in cellulose research and technology was essentially empirical in nature. Since that time, however, the theoretical concepts concerning

cellulose and other high polymers have been well developed. The modern picture of cellulose as a chain macromolecule has resulted in an understanding of the chief reasons for the chemical and physical behavior of this substance and of its derivatives. Many excellent opportunities exist for fundamental research in this field, and it is hoped that this book will be a contributing factor to such developments. It is not unreasonable to predict that, inasmuch as most of the great industrial developments which have expanded the uses of cellulose and cellulose derivatives were by necessity based on an empirical approach alone, the available modern and well-substantiated theories will lead to advancements along new and wider fronts.

Chapter I

OCCURRENCE OF CELLULOSE

OCCURRENCE OF CELLULOSE

KYLE WARD, JR.

Cellulose is the most abundant of all naturally occurring organic compounds and probably makes up at least a third of all the vegetable matter in the world. It is the main constituent of the cell walls of the higher plants, having received its name for this reason.[1] Its existence in the lower orders of the vegetable kingdom has been disputed, but there is good evidence that it does occur in many of the lower species.

For instance, cellulose has been reported absent in the tubercle bacillus[2] and in several other bacteria.[3] It is certainly present, however, in *Acetobacter xylinum*,[4, 5] where it has been identified by means of all the better known techniques, including the x-ray diffraction pattern and acetolysis to cellobiose octaacetate.

Similarly, cellulose has been reported absent or present only in very small amounts in the algae, fungi, and lichens.[6] It has been identified in *Laminaria digitata*, however, by the formation of methyl and acetyl cellulose, by the viscose reaction, and by hydrolysis to glucose.[7] Using the last reaction, as well as a study of pyrolysis products, it has been reported[8] in two other species of *Laminaria* and two of *Fucus*, including the same species used in the negative report just cited.[6] Miwa reports that cellulose is lacking in *Porphyra*, but constitutes 5 to 15% of most brown algae and 1.5 to 3% of the Florideae.[9] In this connection it should be pointed out that the structural material in marine algae is sufficiently similar to

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[1] A. Payen, *Compt. rend.*, **7**, 1052, 1125 (1838).

[2] O. Binder, *Compt. rend.*, **197**, 197 (1933).

[3] C. van Wisselingh, *Pharm. Weekblad*, **53**, 1069, 1102 (1916); *Chem. Abstracts*, **10**, 3090 (1916).

[4] W. K. Farr and S. H. Eckerson, *Contrib. Boyce Thompson Inst.*, **6**, 189 (1934).

[5] H. Hibbert and J. Barsha, *Can. J. Research*, **5**, 580 (1931).

[6] R. S. Hilpert, D. Becker, and W. Rossée, *Biochem. Z.*, **289**, 179 (1937).

[7] T. Dillon and T. O'Tuama, *Sci. Proc. Roy. Dublin Soc.*, **21**, 147 (1935); *Chem. Abstracts*, **29**, 2735 (1935).

[8] G. Viel, *Compt. rend.*, **208**, 532 (1939).

[9] T. Miwa, *Japan. J. Botany*, **11** (1), 41 (1940); *Biol. Abstracts*, **16**, 499 (Abstract No. 5517) (1942).

cellulose that its use in paper pulp has been seriously considered.[10, 11, 1] Cellulose has been reported in yeast, the identification consisting of insolubility in alkali and hydrolysis to glucose.[13] Using staining reactions, cellulose was identified in the lower fungi in the Oömycetes and in a new species, *Rhizidiomycetes bivellatus*, among the Chytridiaceae. No cellulose was found in other Chytridiaceae, Blastocladiaceae, Ascomycetes,[14] or Actinomycetales.[15]

Among the mosses and ferns, cellulose has been quite definitely identified in brake fern[16] and in hair cap moss,[17] using the formation of cellobiose octaacetate as evidence. The same investigators have also established the presence of cellulose in Spanish moss, which is not a true moss, using the same criteria.[18]

These references by no means cover the field of cellulose in the lower plants. They merely cite examples showing how well authenticated its existence is in certain cases. Where the less specific microchemical tests of the botanist are used as criteria, cellulose is reported from nearly every type of vegetable life.

As an example, a recent article[19] reports the observation of cellulose particles, using the sulfuric acid-iodine test, in plants from four families of fungi (in stipes, gills, basidiospores, sporangiophores, mycelia, and spores), from twenty families of algae (in cell walls and cytoplasm), from two families of liverworts (in rhizoids, thalli, gemmae, spore mother cells, and tetrads), from three families of mosses (in leaves, paraphyses, spores, and stems), and from three families, ten species, of pteridophytes (in spores, sporangia, prothalli, rhizoids, epidermal hairs, leaves, and roots). The higher plants, fifty species, well distributed throughout the various divisions of the spermatophytes, were also investigated. The tissues investigated in the spermatophytes were from all parts of the plant, root, stem,

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[10] V. Hottenroth, *Papier-Fabr.*, **32**, Tech.-wiss. Tl., 337 (1934).

[11] V. de Buen, *Rev. ing. ind.*, 1, No. 6, 5; No. 8, 12 (1930); *Chem. Abstracts*, **25**, 1937 (1931).

[12] T. Dillon, D. T. Flood, V. C. Barry, and P. O'Muineacáin, Brit. Patent 508,671 (July 4, 1939).

[13] E. Salkowski, *Z. physiol. Chem.*, **114**, 31 (1921).

[14] K. Nabel, *Arch. Mikrobiol.*, **10**, 515 (1939); *Chem. Abstracts*, **35**, 5147 (1941).

[15] O. V. Plotho, *Arch. Mikrobiol.*, **11**, 33 (1940); *Chem. Abstracts*, **35**, 5147 (1941).

[16] W. M. Harlow and L. E. Wise, *Am. J. Botany*, **25**, 217 (1938).

[17] W. M. Harlow and L. E. Wise, *Am. J. Botany*, **25**, 760 (1938).

[18] L. E. Wise and A. Meer, *Proc. Florida Acad. Sci.*, **1**, 131 (1936); *Chem. Abstracts* **32**, 2984 (1938).

[19] F. L. Barrows, *Contrib. Boyce Thompson Inst.*, **11**, 61 (1939).

af, flower, and fruit; they included such differentiated materials as cell alls, epidermis, hairs, cortex, wood, bast fibers, buds, coleoptiles, petioles, eins, corn silk, anthers, pollen, calyxes, pistils, corollas, peduncles, husks, nd seed.

A. SIGNIFICANCE OF TERMS

The word "cellulose," when used in a technical sense, does not mean exctly the same thing as when used to denote an organic compound. Techically, "cellulose" denotes the residues obtained by subjecting vegetable naterials to certain pulping processes. These pulps consist in the main of

TABLE 1

DEGREE OF POLYMERIZATION OF SOME NATURAL CELLULOSES
(As Calculated from Viscosity Data of Staudinger and Feuerstein[20])

Source of cellulose	Degree of polymerization
Cotton lint	2020
Linters	1440
Ramie	2660
Flax (three varieties)	2190, 2390, 2420
Hemp (three varieties)	2200, 2200, 2300
Manila hemp	1990
Sisal hemp	2160
Jute	1920
Papyrus	2000
Nettle	2280
Acetobacter xylinum	1890

cellulose and closely related materials, but may differ in both amount and nature of the noncellulosic constituents. The content of cellulose varies with the pulping process and with the material used. Cellulose, chemically speaking, is a polysaccharide of sufficient chain length to be insoluble in water or dilute acids and alkalies, consisting of glucose anhydride units linked together through the 1 and 4 carbon atoms with a β-glucosidal linkage, and giving a typical x-ray diagram.

This must not be understood to mean, however, that cellulose consists of identical molecules, as do the compounds of lower molecular weight. The number of glucose anhydride units per molecule may vary over a wide range. A given sample of cellulose will thus contain many molecules of different lengths. The so-called degree of polymerization represents an

[20] H. Staudinger and K. Feuerstein, *Ann.*, **526**, 72 (1936).

average value for the number of glucose anhydride units in the molecule Natural celluloses have a degree of polymerization of 1500–2500,[20] or even higher,[21, 22] as shown in Table 1, but hydrolyzed material may drop into the so-called "mesocolloid" range, 50–500, and still retain the characteristics of cellulose. The methods of determination of degree of polymerization and the discrepancies between methods will be discussed in Chapter IX, C.

It was formerly held that the differences between cellulosic pulps from different sources were due to differences in the structure of the cellulose present, but today it appears more probable that these differences are due largely to differences in the noncellulosic ingredients, in the degree of polymerization of the cellulose, and in the physical structure of the individual fibers. Fibers from different sources have markedly different structure as will be seen in the section on microscopy in Chapter III, C.

Alpha-cellulose refers to that portion of industrial cellulose pulps which is insoluble in cold sodium hydroxide of mercerizing strength (17.5 or 18%). Beta-cellulose is soluble in such a solution but is precipitated on acidification, while gamma-cellulose remains in solution on acidification. Beta- and gamma-celluloses are not necessarily true celluloses in the sense that they contain only polymers of glucose anhydride units. They may consist of polymers of other sugars such as the xylans, oxidation products such as oxycellulose, or true cellulose compounds of low molecular weight.[23] The alpha-cellulose fraction, from whatever source derived, probably consists to a very large extent of cellulose as just defined. There are a number of methods, both gravimetric and volumetric, for the determination of alpha-, beta-, and gamma-cellulose.[24]

B. FORMATION OF CELLULOSE

There is no generally accepted theory on the formation of cellulose. According to one hypothesis,[25, 26] cellulose is formed in large plastids occurring in the cytoplasm of the living cell. At a certain stage of development these plastids burst and the cellulose enters the cytoplasm in the form of small ellipsoidal particles 1.5 by 1.1 microns in size. These particles coalesce to form fibrils which in turn build up secondary layers on the cell

[21] E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).
[22] K. Hess and E. Steurer, *Ber.*, **73B**, 669 (1940).
[23] H. Koch, *Papier-Fabr.*, **39**, Tech.-wiss. Tl., 46 (1941).
[24] M. W. Bray, U. S. Forest Products Laboratory, Mimeographed Rept. **R19** (1939).
[25] W. K. Farr, *Nature*, **146**, 153 (1940).
[26] W. K. Farr, *Contrib. Boyce Thompson Inst.*, **12**, 181 (1941).

wall.[4] There has been a great deal of discussion of this hypothesis, both pro and con.[27, 28] Another hypothesis calls for the formation of cellulose on the cell wall. According to one form of this theory,[29] glucose undergoes its first change in the cytoplasm. Further action precipitates a substance termed "amyloid" on the cell wall which undergoes further change to "intercellose" and eventually to cellulose. A review of the theory of cellulose formation in wood has been made by Wislicenus.[30] We have practically no information as to the essential chemical mechanism of the phytosynthesis of cellulose, but it is presumably enzymatic.

C. IDENTIFICATION OF CELLULOSE

The x-ray diagram is the most characteristic test for cellulose.[31, 32] It requires special, expensive equipment, however, which is not universally available. Cellulose exists in more than one crystalline modification, these giving different x-ray patterns. The "normal" pattern is by far the most common in nature. A second pattern can be produced by mercerization with subsequent removal of the alkali. This is called the "mercerized" or "hydrate" pattern.[33] Only one case is recorded[34] where a naturally occurring cellulose gives this x-ray pattern. This is in the genus *Halicystis*. X-ray diagrams give evidence that cellulosic materials contain the recurring cellobiose unit but no evidence of molecular size or distribution.

Acetolysis to cellobiose octaacetate also shows the presence of the cellobiose unit, and this test has been of considerable use in identifying cellulose.

Another group of chemical methods includes those which indicate the presence of glucose as the only unit in the molecule. This is also useful, but not quite as distinctive as the preceding, since there are other polysaccharides, such as starch and glycogen, which are also made up exclusively of glucose residues. The simplest method of this type is acid hydrolysis. Another method consists of methanolysis of the fully methylated substance. If carefully carried out, this method gives other information as well. The presence of methyl trimethylglucosides other than methyl 2,3,6-trimethyl-

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[27] D. B. Anderson and T. Kerr, *Ind. Eng. Chem.*, **30**, 48 (1938).

[28] W. K. Farr, *J. Phys. Chem.*, **42**, 1113 (1938).

[29] M. Lüdtke, *Biochem. Z.*, **233**, 1 (1931).

[30] H. Wislicenus, *Papier-Fabr.*, **31**, Fest- u. Auslands-Heft, 65 (1933).

[31] O. L. Sponsler and W. H. Dore, *Fourth Colloid Symposium Monograph.* Chemical Catalog, New York, 1926, p. 174.

[32] W. A. Sisson, *Chem. Revs.*, **26**, 187 (1940).

[33] W. A. Sisson and W. R. Saner, *J. Phys. Chem.*, **45**, 717 (1941).

[34] W. A. Sisson, *Contrib. Boyce Thompson Inst.*, **12**, 31 (1941).

glucoside or of lower methyl derivatives would show the presence of polysaccharides other than cellulose, while the amount of methyl tetramethylglucoside present has been used as an indication of the average molecular size.

The identification of cellulose microscopically is almost a separate problem. Since cellulose is anisotropic, the double refraction and the refractive indices are used as evidence, although there has been disagreement as to the correct values for the latter.[4, 27, 35, 36] Color tests with iodine and zinc chloride, iodine and sulfuric acid, or iodine and phosphoric acid are also used.[4] It has been shown, however, that polysaccharides other than cellulose may give these tests[37] and also that poorly crystallized cellulose is stained by iodine alone,[38] similar to starch. Certain dyes, such as Congo red, have also been recommended as stains. However staining reagents are not, in general, specific indicators of the presence of cellulose.[39, 40]

Any of these tests should be combined, however, with two very simple determinations: insolubility in hot water and solubility in cuprammonium hydroxide. The solubility characteristics set up a certain rough limit for the chain length. This is necessary as it is obvious that there must be a lower limit, admittedly ill-defined, for molecular size, below which a polyglucosan is no longer cellulose.

That these characteristics may still be insufficient will be shown later in the discussion of animal cellulose or tunicin. Whether or not the differences in such a case as animal cellulose are real or whether they are due to contamination cannot be stated at this time.

D. INDUSTRIAL USES OF CELLULOSE

Modern industry requires vast amounts of cellulose. The paper and pulp industry depends upon cellulosic raw materials. In the textile industry all the important natural vegetable fibers are cellulosic in nature. Among the synthetic fibers, viscose, cuprammonium, and cellulose acetate rayons are all prepared from highly purified cellulose pulps. Large amounts of cellulose and cellulose derivatives are also used in explosives, in films and foils, in plastics, in protective coatings, in adhesives, in textile sizes, and in

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[35] A. Frey, *Kolloidchem. Beihefte*, **23**, 40 (1926).

[36] A. Frey-Wyssling and K. Wuhrmann, *Helv. Chim. Acta*, **22**, 981 (1939).

[37] M. Lüdtke, *Ann.*, **456**, 201 (1927).

[38] A. Frey-Wyssling, *Verh. schweiz. Naturforsch. Ges.*, **1939**, 67; *Chem. Abstracts*, **35**, 6442 (1941).

[39] W. M. Harlow, N. Y. State Coll. of Forestry, *Tech. Pub.* **26**, III (1928).

[40] W. M. Harlow, *Paper Trade J.*, **112**, 31 (June 5, 1941).

many other important industrial products. Cellulose and vegetable materials containing cellulose are also capable of being used for many purposes in which it is broken down chemically Normally this is uneconomical as there are more suitable raw materials. However, in countries with insufficient starch or sugar, glucose and alcohol can be produced from cellulose; cellulosic wastes, such as sawdust, are used for the production of oxalic acid; and destructive distillation of wood was for a long time the chief source of methanol and acetic acid. Moreover, in the form of wood or agricultural residues cellulose is probably the oldest fuel.

The industrial requirements of cellulose are met by materials obtained from many different botanical sources. Woody matter, seed hairs, bast fibers, stalks, hulls, straw, even marine plants and peat are used for various purposes. Only a brief introductory discussion of these sources is in order here, as the preparation of cellulose from its important commercial sources will be described in detail in Chapter VI.

E. SOURCES OF CELLULOSE

1. Wood Cellulose

Wood is found all over the world, being the substance of which the branches and trunks of the higher plants are composed. There are two main classes of wood. The hardwoods, or deciduous woods, such as oak, are generally composed of closely packed cells with thick walls, while the softwoods, or coniferous woods, such as pine or cedar, are usually composed of large cells with thin walls. The composition of wood varies with the species and also with the part of the tree from which it is taken. In round numbers, on a dry basis, it contains 40 to 50% cellulose, 20 to 30% lignin, and 10 to 30% hemicelluloses and polysaccharides other than cellulose. Resins, gums, proteins, mineral compounds, etc., are also present. Wood is the most widely used of all the cellulosic materials.

The utilization of wood as a material for construction, for ornament, or for fuel is outside the scope of this book, but in passing it might be stated that practically every species is used for one or more of these purposes. The present discussion deals more directly with the fields in which cellulose is freed from noncellulosic components to produce a cellulose pulp. The pulp industry prepares the raw material for most of the viscose rayon and paper and for much of the nitrocellulose now being produced.

Several kinds of wood are used in the preparation of wood pulp. The most common are the pines (*Pinus* sp.), spruces (*Picea* sp.), firs (*Abies* sp.), beeches (*Fagus* sp.), poplars and aspens (*Populus* sp.), and hemlock (*Tsuga*

sp., especially *Tsuga canadensis*). There are three main chemical pulping processes. The sulfite process is used mostly on the Northern conifers, chiefly spruce, hemlock, and fir, although recently it has also been adapted for pulping young Southern pines which are free of heartwood; the sulfate (kraft) process is also used chiefly on coniferous woods, finding, for example, wide application in the southern part of the United States since it is well adapted to the Southern pines; the soda process is used on such hardwoods as aspen, gum, poplar, birch, and willow. The wood cellulose used in chemical industries (the so-called "dissolving pulps") is usually obtained by the sulfite process.[41, 42]

Such parts of the plant as bark, leaves, pith, knots, and trimmings may be more correctly considered as agricultural residues than as wood, but suggestions for their utilization have not been lacking, especially in the field of insulating materials and wallboard.

The magnitude of the wood cellulose industry is hard to appreciate. The United States produced 8,851,740 tons of wood pulp in 1940, while the 1941 production has been estimated at 9,955,000 tons.[43]

2. Seed Hairs

The most important of the seed hairs is cotton. Of all the commercial raw materials for cellulose, the cotton fiber contains the lowest percentage of noncellulosic material, 3 to 15%.[44] This makes purification simpler than for most cellulosic materials.

The cotton plant belongs to the genus *Gossypium*, which has been a difficult genus to classify so that confusion exists in the enumeration and nomenclature of the species. It is probable that practically all the important commercial varieties of cotton are hybrids.[45]

In considering the cotton plant from the standpoint of cellulose, it is necessary to recognize that two types of hair are developed on the cottonseed. The lint fibers are paler, longer, and finer than the fuzz fibers and have a much smaller central canal or lumen. The lint fibers are removed from the seed by ginning. The gin, of course, makes no exact separation between lint fiber and fuzz fiber. Some of the fuzz fibers are long enough to be removed with the lint while some of the lint fibers remain on the seed.

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[41] E. Hägglund, *Holzchemie*. Akademische Verlagsgesellschaft m. b. H., Leipzig, 1939.

[42] L. F. Hawley and L. E. Wise, *Chemistry of Wood*. Chemical Catalog, New York, 1926.

[43] J. Cornell, *Paper Mill News*, **65**, No. 3, 8 (1942).

[44] J. H. Kettering and C. M. Conrad, *Ind. Eng. Chem., Anal. Ed.* **14**, 432 (1942).

[45] H. B. Brown, *Cotton*. McGraw-Hill, New York, 1938.

On leaving the gin, the seed goes to the oil mills. Here the greater part of the remaining fiber is removed. This fiber constitutes cotton linters, most of which is utilized for the manufacture of chemical cellulose. The very short residual fuzz is called hull fiber and remains on the hulls after cracking and removal of the meats. Some hull fiber is recovered and purified for cellulose.

The bales of lint cotton leaving the gin are broken up and mechanically cleaned at the textile mills but usually undergo no other purification until after they have been spun into yarn or woven into cloth. The bleaching process usually consists of a water boil, an alkaline boil, and a hypochlorite bleaching with thorough washing to remove the remaining bleaching solution. This relatively mild chemical treatment is sufficient to remove practically all the noncellulosic material from the cotton. A similar chemical treatment performs the same function in the production of chemical cotton from cotton linters. These processes will be described in more detail in Chapter VI, B.

It has been proposed that the whole cotton plant be utilized for cellulose pulps,[46, 47] since not only the seed hairs, but also the stalks, burs, leaves, etc., are cellulosic in nature. Investigations of this proposal have not progressed past the experimental stage as there are still both economic and technical difficulties in the way of commercial exploitation. It has been postulated that the extracted oil might pay the total cost of production of whole cotton which would leave the residual pulp as a very cheap source of cellulose. However, the industrial value of oil extracted from the whole cotton plant has not yet been established. Experience in pulping other materials, moreover, has shown that the material should be as uniform in composition and particle size as possible, and it seems likely that the change to industrial scale will involve difficulties due to the nonuniformity of raw material. These and similar considerations will make it necessary for further experimentation to be carried out before the proposal becomes industrially attractive.

Estimated figures on cotton production for 1940 are 30,230,000 bales for the world production, of which the United States was responsible for 12,566,000 bales. In addition to this, the United States produced 1,200,000 running bales of cotton linters.[48]

There are no other seed hairs which have found application to the same extent as cotton. Of increasing importance is the consumption of the

[46] A. R. Macormac and F. K. Cameron, *Ind. Eng. Chem.*, **29**, 96 (1937).

[47] F. K. Cameron, *Manufacturers Record*, **110**, 30 (1941).

[48] U. S. Dept. Agr., *Agricultural Statistics*. Govt. Printing Office, Washington, 1941.

kapok fiber, from *Ceiba pentandra*.[49] Kapok fiber is widely used as a stuffing material particularly for life preservers because of its buoyancy and resistance to moisture. It contains from 55 to 65% cellulose on a moisture-free basis, but is not used as a source of cellulose pulp. Bombax cotton obtained from several species of *Bombax* is used for wadding and upholstering. Seed hairs from certain species of *Asclepias*, such as the milkweed (*A. syriaca*), are also used in upholstery, as is the pulu fiber from fern trees of the *Cibotium* genus.[50]

3. Bast Fibers

The bast fibers are the long fibers of the inner bark of various plants. They include flax, hemp, jute, ramie, and many other less important fibers. While widely used in textiles and paper, they have found no industrial utilization for pulps high in alpha-cellulose. The yields of the bast fibers are very small, based on the green weight of the stems.

The flax plant (*Linum usitatissimum*) is the source of the important textile fiber linen, which contains 80 to 90% cellulose. Linseed oil is obtained from the seed of the flax plant. However, the fiber is most easily obtained from plants which have not fully matured and the best oil from completely ripened plants. Flax therefore is grown either as seed-flax or fiber-flax. Distinct varieties have been developed and only one major product is obtained from either crop. However, the short fiber separated from the seed-flax straw is utilized by the paper industry. Flax fiber, like the other bast fibers, is usually freed from the woody portion of the stem by a retting process. The world production of textile flax in 1938 was 896,000 tons.[48]

Many different vegetable fibers are loosely referred to as hemp. The common hemp is *Cannabis sativa*, the same plant which produces the narcotic marihuana. In the United States its growth is restricted for this reason. Bleached hemp contains approximately the same amount of cellulose as bleached linen and is similarly produced and processed. Hemp is widely used for ropes and cordage and for bagging, although other fibers have replaced it to a large extent. Other bast fibers bearing the name of hemp include Sunn hemp (*Crotalaria juncea*), also called sunn, and gambo or ambari hemp (*Hibiscus cannabinus*), better known as kenaf. The 1938 world production of true hemp was estimated at 365,000 long tons.[51]

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[49] S. J. Zand, *Kapok*. S. J. Zand, New York, 1941.

[50] J. M. Matthews, *Textile Fibers*. 4th ed., John Wiley, New York, 1924.

[51] *Commodities in Industry*. Prepared and published by Commodity Research Bureau, Inc., New York, 1940

Jute is obtained from various species of *Corchorus*, especially from *Corchorus capsularis*. It has not been of much importance for the paper and pulp industry although jute waste finds some utilization there. It is the cheapest of the textile fibers and is used widely for making sacks and bags. Jute fiber contains less cellulose than the preceding fibers (60 to 70%) and more xylan.[52, 53] In 1940 the jute production of the world was estimated at 2,512,500 tons.[48]

Ramie, China grass, or rhea (there is some confusion as to the names)[50, 54, 55] is obtained from *Boehmeria nivea* (or *Urtica nivea*) and *Boehmeria tenacissima*. Its use as a textile fiber in the Orient dates back several thousand years. It has a high tensile strength and a high luster and is relatively little affected by moisture. However, its separation, purification, and processing are difficult, while its brittleness and inelasticity limit its uses greatly. Purified ramie fiber contains about 85% cellulose.[52, 53] In China where cheap labor is available, very beautiful handmade fabrics are produced from this fiber. It is also exported to other countries and used to a slight extent, largely in admixture with other fibers. Its use in paper has also been slight, being limited to specialty papers requiring high strength. The ramie fiber has been an important factor in elucidating the structure of cellulose, as the fibrils of which the fiber is composed are very highly oriented parallel to the fiber axis, which is responsible for a very clear x-ray diffraction pattern.

The bast fibers of the larger plants have also found some application. In the Orient the tappa or paper mulberry, *Broussonetia papyrifera*,[50] is used widely for paper, and also to a certain extent in textiles. The African baobab (*Adansonia digitata*)[50] and the willow (*Salix* sp.) have been used for paper-making.[56] The bast of the castor bean plant (*Ricinus communis*) has been recommended for cordage.[57]

4. Leaf Fibers

Many of the vegetable fibers used in industry are obtained from the leaves of plants. The most important of these are the so-called hard fibers which are extensively used for cordage. Many of these are roughly and

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[52] A. G. Norman, *Biochem. J.*, **30**, 831 (1936).

[53] S. G. Barker, *J. Textile Inst.*, **30**, P273 (1939).

[54] G. L. Carter and P. M. Horton, *Ramie*. Louisiana State Univ. Studies No. **26**, L. S. U. Press, Baton Rouge, 1936.

[55] B. B. Robinson, U. S. Dept. Agr., *Dept. Circ.* **585** (1940).

[56] M. Lüdtke, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 65 (1938).

[57] W. W. Floyd, *Southern Pulp and Paper J.*, **3**, No. 2. 7 (1940).

improperly classed as "hemps." In 1938 the world production of hard fiber hemps was 467,000 long tons.[51]

The most important hard fiber is probably abacá or Manila hemp which is obtained from the leaf stalks of *Musa textilis*.[50] The fiber is separated mechanically from the pulp, purified, and sun-dried. To a much smaller extent other species of *Musa* have been utilized. The banana, *Musa sapientum*,[58, 59, 60] has received a good deal of study due to its extensive cultivation and the availability of large amounts of waste.

Another important hard fiber is sisal hemp which is obtained from the leaves of *Agave sisalana*. There are many other varieties of *Agave* and related genera used for fiber, most of them coarser than true sisal. These include maguey, henequen, and cantala, all true agaves. Other hard fibers include phormium, also known as New Zealand flax or New Zealand hemp (*Phormium tenax*) and piteira or Mauritius hemp, which is obtained from *Furcraea gigantea* and other aloe plants.[50]

Another group of leaf fibers used for belts, coarse fabrics, and cordage is the bromelia fibers.[50] These are derived from various species of *Bromelia*. The best known of these is called wild pineapple and is obtained from *Bromelia pinguin*. The leaf of the true pineapple (*Ananas comosus*) is used also in textiles.[50] The fiber from the leaf of several species of yucca has been used for cordage and for paper.[56] Another important leaf fiber used for cordage and paper is caroa (*Neoglaziovia variegata*).

There are a great many other leaf fibers which find limited use, some of which will be mentioned in the next subdivision.

5. Grasses, Straws, and Agricultural Residues

Since cellulose is the major constituent of the cell wall of plant life, it is clear that those plants which have no industrial utilization, as well as the residual wastes from utilized plants, form a huge potential source of cellulose. The annual production of agricultural residues in this country has been estimated at 173,000,000 tons on a moisture-free basis.[61]

By far the most important of these wastes and residues, as far as their present utilization is concerned, belong to the grass family. The cereal straws in particular have long been used in the manufacture of paper and

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[58] L. Robinson-Gomez and L. L. Leonio, *Univ. Philippines Nat. and Applied Sci Bull.*, **6**, 97 (1938); *Chem. Abstracts*, **32**, 8774 (1938).

[59] M. J. Stacom, Brit. Patent 492,524 (Sept. 16, 1938).

[60] F. H. de Balsac, *Bull. agence gén. colonies (Paris)*, **25**, 252 (1932); *Chem. Abstracts*, **26**, 3108 (1932).

[61] *Senate Document* No. 65, 76th Congress, 1st Session, Washington (1939).

paperboard.[62] In fact, the use of straw in paper products antedates the use of wood pulp by many centuries, since the former dates back to our earliest records of paper while the latter came into use only in the last century. Local production governs the type of straw used; in the United States wheat straw is most used; in the Orient, rice straw. The preparation of rayon cellulose from cereal straws is being suggested in many of the countries now unable to obtain pulp.[63]

Another material extensively used for the manufacture of wallboard and insulation board is bagasse which consists of the crushed stalks of the sugar cane (*Saccharum officinarum*) after the juice has been expressed.[62, 64] Bagasse is a particularly promising material since the collection is carried out by the sugar industry and the residue is available in a clean condition at the mills. Pulp of high alpha-cellulose content has been produced from bagasse on a pilot-plant scale.[65] Similar utilization of sorgo bagasse[66] has been recommended. The pulping of grain sorghum residues has also been investigated and the production of satisfactory paper and chemical pulp from several varieties has been reported.[67, 68]

Cornstalks have also been widely investigated.[69] As with most stalks, problems of collection and of cleaning must be solved before any extensive utilization can take place. However, cornstalks have been used industrially in the manufacture of insulating board,[70, 71, 72] and their use for the preparation of cellulose for rayon and explosives is reported from Italy.[67]

Paper pulp has been made for some time[73] from esparto grass (*Stipa tenacissima* and *Lygeum spartium*) which grows in the Mediterranean

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[62] E. C. Dryden, S. I. Aronovsky, and T. D. Jarrell, *Paper Ind. Paper World*, **21**, 972, (1939).

[63] E. Goethals, *Rusta-Rayonne*, **13**, 381 (1938); *Chem. Abstracts*, **33**, 375 (1939).

[64] E. C. Lathrop, *Ind. Eng. Chem.*, **22**, 449 (1930).

[65] S. I. Aronovsky and D. F. J. Lynch, *Ind. Eng. Chem.*, **30**, 790 (1938).

[66] C. Levi and E. Debenedetti, *Ind. carta*, **5**, 294 (1938); *Chem. Abstracts*, **33**, 4017 (1939).

[67] A. Contardi and B. Ciocca, *Ricerca sci.*, **8**, II, 155 (1937); *Chem. Abstracts*, **34**, 4899 (1940).

[68] E. Munds and Yung-Hui Chang, *Zellstoff Faser*, **32**, 170 (1935); *Chem. Abstracts*, **30**, 2752 (1936).

[69] O. R. Sweeney and L. K. Arnold, Iowa Eng. Expt. Sta., *Bull.* **98** (1930).

[70] C. E. Hartford, *Ind. Eng. Chem.*, **22**, 1280 (1930).

[71] M. Krajčinovič, J. Zalesow, and F. Szücs, *Angew. Chem.*, **53**, 475 (1940).

[72] B. Wingfield, T. R. Naffziger, E. R. Whittemore, C. B. Overman, O. R. Sweeney, and S. F. Acree, U. S. Bur. Standards, *Misc. Pub.* No. **M123** (1936).

[73] E. Sutermeiste *Chemistry of Pulp and Papermaking*. 3rd ed., John Wiley, New York. 1941.

region. This is also known as alfa fiber and has been recommended as a promising material for the manufacture of rayon cellulose.[63, 74] Numerous other tropical grasses have also been tried out as sources of pulp, many of them with promising results.

Reeds (*Arundo donax*[75] and various species of *Phragmites*) and the related cattails (*Typha* sp.)[58] are also coming in for a great deal of attention in the search for cellulose sources. The typha fiber is reported to yield a better fiber than do the reeds.

Another plant of the grass family from which a good grade of paper pulp can be obtained is the bamboo (*Bambusa*, *Arundinaria*, *Dendrocalamus*, and related genera). It has, in fact, been predicted that the woody stalks of the bamboo will form the "paper fiber of the future."[76]

In addition to stalks and straws, other products from grains and grasses have been examined. Corncobs[77, 78] and rice hulls[79] are two good examples. An edible cellulose for incorporation into breakfast foods has been manufactured from rice hulls, and insulating board has been produced experimentally from corncobs.

Closely allied to the grasses is the papyrus plant (*Cyperus papyrus*)[50] which was one of the earliest raw materials for paper. In preparing the old papyri from this plant, the individual fibers were not isolated but thin sheets of the pith were united in a manner similar to the manufacture of plywood.

A great many industrial fibers are derived from plants of the palm family. One of the more important is coir fiber, which is derived from the husks of the cocoanut (*Cocos nucifera*). Others include raffia from the leaves of *Raphia* sp. and piassava fiber from *Attalea funifera* (piassava fibers are also obtained from other palms, such as *Raphia vinifera*).[50] The saw palmetto (*Serenoa repens*) has also been suggested as a fiber plant,[62] while the cabbage palmetto (*Sabal palmetto*) has been utilized for brush fiber for some time.

The list of minor vegetable fibers is long and it would be outside the scope of this chapter to attempt to name all of them. The cellulose content of a large number of minor fibers has been determined by Norman.[80] An idea of the variety of plants exploited may be gained by listing just a few more

[74] G. Cuchiara, *Ind. carta*, 6, 173 (1939); *Chem. Abstracts*, **34**, 7597 (1940).
[75] A. C. Rogers, *Pulp Paper Mag. Can.*, **41**, 607 (1940).
[76] C. G. Schwalbe, *Proc. World Eng. Congr., Tokyo, 1929*, **31**, 497 (1931).
[77] C. E. Hartford, U. S. Bur. Standards, *Misc. Pub.* No. **108** (1930).
[78] O. R. Sweeney, Iowa Eng. Expt. Sta., *Bull.* **73** (1924).
[79] E. R. Harding, *Ind. Eng. Chem.*, **20**, 310 (1928).
[80] A. G. Norman, *Biochem. J.*, **31**, 1575 (1937).

which might fall under the head of weeds or wastes, but which have actually been used as textile or paper fibers: nettle fiber (*Urtica dioica*),[56] hop fiber (*Humulus lupulus*),[56] Spanish moss (*Tillandsia usneoides*),[81] several marine plants and seaweeds[50] (*Zostera marina, Macrocystis pyrifera, Posidonia australis*), and extracted licorice root,[82] rape wastes, and thistle fiber.[83]

Many other products have been considered as sources of cellulosic fibers: peanut hulls,[84] soybean stems,[85] oat hulls,[62] cacao shells,[86] olive pits,[87] cacti,[88] water hyacinths, [89, 90] coffee beans,[91] sunflower stalks,[92] castor bean stalks,[57] and various tree, vine, or bush trimmings.[93] Curtailment of cellulose shipments to those countries with no good domestic source has produced an added incentive in the past few years to experiment with new sources and to repeat former experiments. From Germany, for instance, come reports of large-scale cellulose production from potato tops and stems[94, 95] and of the production of cellulose satisfactory for rayon or chemical conversion from the shells of the cacao bean.[86]

6. Cellulose Outside the Vegetable Kingdom

Cellulose is not confined to the vegetable kingdom. It is also found in the mineral and animal kingdoms. In the former, to be sure, it occurs in products of vegetable origin, being found in fossil woods,[96] in peat,[97] and in

[81] A. Meer and L. E. Wise, *Ind. Eng. Chem., News Ed.*, **13**, 263 (1935).

[82] P. A. Houseman and H. T. Lacey, *Ind. Eng. Chem.*, **21**, 915 (1929).

[83] G. Abrahamson, *Chem. Eng. News*, **20**, 121 (1942).

[84] D. F. J. Lynch and M. J. Goss, *Ind. Eng. Chem.*, **22**, 903 (1930).

[85] M. Arakawa and K. Akagi, *Rayon World (Japan)*, **5**, No. 8, 4 (1937).

[86] R. Garascia, *Gordian, Z. Gewinnung, Handel u. Verarbeit. Kakao Zucker u. verwandten Erzeug.*, **46**, 17 (1940); *Chem. Abstracts*, **34**, 5656 (1940).

[87] T. Malanos, *Z. Papier, Pappe, Zellulose, Holzstoff*, **57**, 206 (1939); *Chem. Abstracts*, **35**, 5312 (1941).

[88] F. Deplano, *Rend. seminar. facoltà sci. univ. Cagliari*, **2**, 15 (1932); *Chem. Abstracts*, **28**, 5977 (1934).

[89] P. N. Sen-Gupta and H. K. Sen, *Science and Culture*, **3**, 442 (1938); *Chem. Abstracts*, **32**, 3605 (1938).

[90] M. A. Azam, *Science and Culture*, **6**, 656 (1941); *Chem. Abstracts*, **36**, 267 (1942).

[91] C. E. Nabuco de Araujo, Jr. and H. S. Polin, *Ind. Eng. Chem., News Ed.*, **19**, 877 (1941).

[92] H. Rauch, *Angew. Chem.*, **53**, 568 (1940).

[93] T. L. Crossley, *Pulp Paper Mag. Can.*, **39**, 568 (1938); *Chem. Abstracts*, **32**, 8137 (1938).

[94] P. Reinhold, *Vierjahresplan*, **4**, 699 (1940); *Chem. Abstracts*, **35**, 2717 (1941).

[95] M. Lüdtke, *Cellulosechem.*, **18**, 5 (1940).

[96] W. A. Gortner, *J. Am. Chem. Soc.*, **60**, 2509 (1938).

[97] R. Potonié and W. Benade, *Braunkohle*, **28**, 335 (1929); *Chem. Abstracts*, **23**, 4552 (1929).

certain types of lignite.[98] There is practically none in bituminous coal. Peat and lignite fiber have found some utilization in paperboard,[99] in insulating sheets,[100, 101] and even in textiles.[50] There is also a "mineral cellulose," sapperite,[101, 102] which is produced from fossil vegetable matter and is found associated with lignite. It consists of white to light-brown fibers soluble in cuprammonium solution. It burns, leaving a light ash, and gives a blue coloration with the zinc chloride-iodine reagent.[103] The existence of cellulose in these materials is evidence of its great stability under the proper conditions. There is no record of cellulose being found in connection with any of the great petroleum deposits, which may be of animal origin rather than vegetable. However, cellulose has been reported in sapropel,[104] which has been suggested as an intermediate stage in the formation of petroleum.

Cellulose has also been reported in the animal kingdom. At least a material is found which gives the same x-ray pattern as cellulose[105] and can be acetolyzed or hydrolyzed to the same products.[106] It differs from cellulose apparently only in yielding different volumes of gas on destructive distillation.[107] This material, called tunicin or animal cellulose, is obtained from the outer mantles of certain marine organisms belonging to the class of the *Tunicata*, such as *Phallusia mamillata*, *Polycarpa varians*, and *Ascidia mentula*.[108] It is either an insufficiently purified true cellulose or a compound very closely related chemically to cellulose.

7. Lichenin

No discussion of the natural occurrence of cellulose would be quite complete without some mention of lichenin. This important constituent of the cell wall of Iceland moss (*Cetraria islandica*) has many of the characteristics of cellulose. It cannot only be quantitatively hydrolyzed to glucose,[109] but

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[98] E. Opfermann and G. Rutz, *Papier-Fabr.*, **28**, Tech.-wiss. Tl., 780 (1930).

[99] R. Beyschlag, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 105 (1938).

[100] A. Patla, *Przeglad Górnicza-Hutniczy*, **31**, 352 (1939); *Chem. Abstracts*, **35**, 4937 (1941).

[101] K. Overlack, *Wochbl. Papierfabr.*, **72**, 33 (1941); *Chem. Abstracts*, **35**, 4593 (1941).

[102] W. Gothan, *Braunkohle*, **21**, 400 (1922); *Chem. Abstracts*, **18**, 211 (1924).

[103] H. Meixner, *Zentr. Mineral. Geol.*, **1938A**, 208; *Chem. Abstracts*, **32**, 6983 (1938).

[104] E. I. Kazakov and B. A. Tovbin, *Trudy Lab. Genez. Sapropelya*, **1939**, No. 1, 165; *Chem. Abstracts*, **34**, 5710 (1940).

[105] R. O. Herzog and H. W. Gonell, *Z. physiol. Chem.*, **141**, 63 (1924).

[106] L. Zechmeister and G. Tóth, *Z. physiol. Chem.*, **215**, 267 (1933).

[107] G. Viel, *Compt. rend.*, **208**, 1689 (1939).

[108] R. Sutra, *Compt. rend.*, **195**, 181 (1932).

[109] M. Hönig and S. Schubert, *Monatsh.*, **8**, 452 (1887).

also, by the use of enzymes free from cellobiase, can be converted quantitatively to cellobiose.[110] It can be methylated to a trimethyllichenin[111] (methoxyl content 45.5%) which yields 2,3,6-trimethylglucose and a small amount of tetramethylglucose on hydrolysis. These facts all point to a structure very similar to that of cellulose. But, on the other hand, lichenin is soluble in hot water and is extracted from Iceland moss in this way. Were this the only difference, lichenin might be considered a cellodextrin, as, indeed, some have so considered it. However, there are other differences, such as the x-ray diagram,[112] which resembles, but is not identical with, that of cellulose hydrate. The molecular size, calculated from the amount of tetramethylglucose formed, is higher than the solubility in hot water would indicate, as cellodextrins with even lower degrees of polymerization are still insoluble. The optical rotations of the acetate and the methyl ether are also anomalous. Various hypotheses have been advanced for the structure of the lichenin molecule. It may be a branched molecule if the branching does not occur too often to invalidate the methanolysis results. Another possibility[111] is the alternating recurrence of 1,1- and 4,4-linkages in the molecule.

F. NATURAL OCCURRENCE OF COMBINED CELLULOSE

Whether or not there is any natural occurrence of chemical compounds of cellulose is still a moot point. Combination of cellulose with lignin or with xylan are two possibilities which have been extensively studied. The status of these two possibilities will be discussed in Chapter II. Of the compound celluloses postulated by early workers (lignocellulose, pectocellulose, cutocellulose), lignocellulose is the only one where there is good evidence for its existence, yet even here the evidence is conflicting.

Cork was believed for some time to contain esters of cellulose with the higher fatty acids.[113] More recent work[114, 115, 116] has tended to show that the acids in cork are not combined chemically with the cellulose, as these esters have been synthesized and do not have the properties of cork.

In the possibilities just discussed, there is no marked difference in physi-

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[110] H. Pringsheim and W. Kusenack, *Z. physiol. Chem.*, **137**, 265 (1924).

[111] K. Hess and L. W. Lauridsen, *Ber.*, **73B**, 115 (1940).

[112] R. O. Herzog, *Z. physiol. Chem.*, **152**, 119 (1926).

[113] A. Grün and F. Wittka, *Z. angew. Chem.*, **34**, 645 (1921).

[114] P. Karrer, J. Peyer, and Z. Zega, *Helv. Chim. Acta*, **5**, 853 (1923).

[115] F. Zetzsche and G. Rosenthal, *Helv. Chim. Acta*, **10**, 346 (1927).

[116] A. Madinaveitia and T. Catalán, *Bol. acad. cienc.* (*Madrid*), **1**, No. 2, 9 (1935); *Chem. Abstracts*, **30**, 3022 (1936).

cal properties to indicate a chemical rather than a physical combination. A somewhat different case is met with in certain plant mucilages, which are water-soluble, but on hydrolysis yield an insoluble residue which has been considered as cellulose. There is reason to consider some of these materials as substances related to cellulose rather than as true cellulose, but the relation in some cases must be very close indeed.

Quince-seed mucilage (*Cydonia vulgaris*) is a good example. The mucilage can be extracted with cold water and is apparently a neutral salt, the free acid of which is insoluble in water, as it can be precipitated by acidification and will redissolve only if the mixture is made slightly alkaline. Hydrolysis with 0.5 *N* H_2SO_4 gives 33% insoluble residue.[117] Part of this is soluble in 17.5% NaOH, but there is a residue of about 24% (based on the original mucilage). Hydrolysis by the Monier-Williams method gives 78% of crystalline glucose (cotton by the same method yields about 91%).[118] Other positive tests for cellulose given by this residue are a blue color with the sulfuric acid and iodine reagent and solubility in cuprammonium hydroxide.

The mucilage from cress-seed (*Lepidium sativum*) contains about 18% of similar material.[119] Hydrolysis by the Monier-Williams method gives 90% of the theory of glucose, determined by the hypoiodite method. This cellulosic residue contains 1.8% of uronic anhydride. This may arise from an impurity or from the main constituent, if, for example, the cellulose has been partially oxidized.

White mustard seed (*Brassica hirta*) contains a similar mucilage. The residue from hydrolysis with dilute sulfuric acid or dilute alkali consists of about 50% of the original mucilage and has the following characteristics of cellulose. It is soluble in concentrated zinc chloride solutions, gives a blue color with zinc chloride and iodine, is acetylated to a triacetate, and can be hydrolyzed by the Monier-Williams method to 72.5% of the theory of glucose, estimated from the reducing power on Fehling's solution. This residue contains 3.4% uronic anhydride groups.[120]

Other mucilages give similar insoluble residues on hydrolysis, usually in smaller amounts, for instance, slippery-elm bark mucilage.[121] A more complete identification of the residue as cellulose might be desirable, as for instance, by the x-ray pattern, but the identification is sufficiently satisfac-

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[117] A. G. Renfrew and L. H. Cretcher, *J. Biol. Chem.*, **97**, 503 (1932).
[118] G. W. Monier-Williams, *J. Chem. Soc.*, **119**, 803 (1921).
[119] K. Bailey, *Biochem. J.*, **29**, 2477 (1935).
[120] K. Bailey and F. W. Norris, *Biochem. J.*, **26**, 1609 (1932).
[121] E. Anderson, *J. Biol. Chem.*, **104**, 163 (1934).

tory to make it clear that the substance must, at least, be closely related to cellulose. The solubility of the mucilages in water is probably due to the presence of the neutral salt groups.

The aim of this chapter has been simply to indicate the extent to which cellulose exists in nature and to point out some of the more interesting sources of this important material. Many of the points touched on will be treated more fully in the later portions of this book.

Chapter II

CHEMICAL NATURE OF CELLULOSE AND ITS DERIVATIVES

A. HISTORICAL SURVEY[1, 2]

CLIFFORD B. PURVES

1. The Concept of Cellulose

Although cotton and linen had been prepared and used from earliest times, the history of the chemistry of cellulose really began in the period 1837–1842 with the investigations of the French agriculturist Anselme Payen. Phillips[3] and Reid and Dryden[4] recently published accounts of Payen's life and researches. Payen studied starch extensively and obtained the enzyme diastase in a crude condition. He clearly recognized that starch was a reserve carbohydrate in plants and formed the opinion that another polysaccharide must be present in the permanent structure of the cell wall. At that time it was customary to extract plant tissue with very mild reagents, such as alcohol and water, and to submit the dried residue to elementary analysis on the assumption that it was a uniform chemical individual. Since the analyses varied from plant to plant, the general impression was that the cell wall consisted of a uniform, woody or ligneous substance peculiar to each species and that it probably contained rather more carbon and hydrogen than a carbohydrate should. Payen rejected the published carbon contents of 47 to 51% for "pure" plant tissues, not because the analyses were faulty, as some thought, but because the plant skeleton must have been insufficiently purified from the woody and fatty materials with which it became incrusted during growth.

In order to mitigate this difficulty during purification, Payen first examined very young plant formations such as seeds, cotton lint, rootlets from herbaceous and woody species, pith from young elder shoots, cucum-

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[1] The first portion of this survey was guided to a considerable extent by that of K. Hess, *Die Chemie der Zellulose*. Akademische Verlagsgesellschaft m. b. H., Leipzig, 1928, pp. 24–36. This work contains many additional references.

[2] See also J. König and E. Rump, *Chemie und Struktur der Pflanzen-Zellmembran*. J. Springer, Berlin, 1914, pp. 5–43, which has many references.

[3] M. Phillips, *J. Wash. Acad. Sci.*, **30**, 65 (1940).

[4] J. D. Reid and E. C. Dryden, *Textile Colorist*, **62**, 43 (1940).

ber tissue, and various leaves as well as a few mosses and lichens.[5] The newly gathered materials were alternately extracted with dilute hydrochloric acid and dilute ammonia, then with water, alcohol, and ether. In every case, the residues contained 43.6 to 45.0% of carbon, 6.0 to 6.5% of hydrogen, and the remainder was oxygen. The residues gave dextrorotatory, gummy materials (dextrins) and eventually a dextrorotatory reducing sugar (dextrose) when boiled with dilute acid,[6] although not when submitted to the action of diastase. These observations convinced Payen that the fibrous warp and woof of all young plant cells consisted of one uniform chemical individual which was a carbohydrate based on glucose residues and isomeric with starch (C, 44.4%; H, 6.2%). As starch gave a blue color with iodine immediately, while the new carbohydrate had first to be somewhat swollen with sulfuric acid, the latter polysaccharide was regarded as the more compact or more highly "aggregated" isomer. Payen named it cellulose.

More drastic methods were necessary to isolate cellulose from mature hardwood (oak). These included the use of nitric acid at 36°C. and the suspension of the finely divided material in boiling caustic soda followed by evaporation almost to dryness. Still more difficulties were encountered with a mature coniferous wood (fir) and resort was made to a chlorination, although Payen noted that the latter method of purification was not without an effect on the cellulose and had to be used with circumspection.

If cellulose was the fundamental, uniform constituent of all plant cell walls, the variation in the over-all composition of plant tissue was caused by variation in the composition of the materials entrapped in the cell wall with the cellulose. In order to check this point, several very finely divided woods were extracted with water, alcohol, weak aqueous acid, and weak alkali.[7] After this preliminary purification, the samples were evaporated with four to five times their weight of strong alkali so that the final temperature was between 150 and 200°C. Two or three extractions left the cellulose pure, and the alkaline extracts on acidification gave fawn-colored precipitates containing 53.7 to 59.4% of carbon depending on their origin. The precipitate from beech was eventually divided into four fractions with the properties shown in Table 1.

[5] A. Payen, *Troisième Mémoire sur les Développements des Végétaux.* Extrait de Mémoires de l'Académie Royale des Sciences. Tome VIII des savants étrangers, Imprimérie Royale, Paris, 1842.

[6] H. Braconnot, *Ann. chim. phys.*, **12**, 172 (1819).

[7] A. Payen, *Quatrième Mémoire sur les Développements des Végétaux.* Extrait de Mémoires de l'Académie Royale des Sciences. Tome VIII des savants etrangers, Imprimérie Royale, Paris, 1842.

Payen clearly recognized that the noncellulose part of wood tissue consisted of several components which varied in their relative amount, and perhaps in their chemical nature, from species to species. Although direct evidence concerning the relationship of these substances to each other in the plant was lacking, Payen expressed the opinion that two or three of them were of an acidic nature and might originally have been combined as acids are combined in fats.

Some botanists soon disputed the uniformity of cellulose[8] and based their opposition on the fact that preparations from different plants varied widely in staining reactions and solubility in cuprammonium. Fremy, who clearly understood the enzymatic conversion of insoluble to soluble pectin forms during the ripening of fruit,[9] was prominent in maintaining that the cell

TABLE 1

NONCELLULOSE FRACTIONS FROM BEECHWOOD (PAYEN[7])

Fraction	% C	% H	Solubility
1	46.1	6.1	Insol. alcohol, ether, ammonia
2	50.1	5.8	Insol. alcohol, ether; sol. ammonia
3	62.3	5.9	Insol. ether; sol. alcohol, ammonia
4	67.9	6.9	Sol. alcohol, ether, ammonia; slightly sol. in water

wall was composed of several substances. These substances included "meta," "para," and other celluloses which differed among themselves in solubility. Pelouze[10] showed that cellulose regenerated from cuprammonium solution was soluble in weaker acid than the very concentrated hydrochloric acid required for the ready solution of the original material. Immediate dilution of the latter solution precipitated cellulose but dilution after one or two days' standing did not do so. Cellulose, when heated in caustic potash at 150 to 190°C., became soluble in cold alkali without losing its capacity to yield reducing sugars on acid hydrolysis. Payen admitted that chemical treatments might modify the physical properties of cellulose by modifying its "state of aggregation." He nevertheless maintained, in opposition to Fremy and others, that naturally occurring specimens were uniform when properly isolated.

Payen's opinion that cellulose was constituted invariably of glucose residues was based of necessity on inadequate data, because really reliable

[8] *Jahresber. der Chem.*, **12**, 529–41 (1859), reviews these discussions in detail.

[9] E. Fremy, *Jahresber. der Chem.*, **1**, 796 (1847–48).

[10] T. J. Pelouze, *Compt. rend.*, **48**, 327 (1859); *J. pharm. chim.*, [3], **35**, 88, 209 (1859).

methods of discriminating one monosaccharide from another were not available until the decade 1880–90. Acid hydrolyzates of many celluloses were then found to contain substantial amounts of galactose, arabinose, mannose, or xylose, as well as glucose. The endosperm of the ivory nut, for example, which Payen had thought an especially pure cellulose, yielded mannose almost exclusively[11] while the cellulose of Iceland moss was eventually recognized as lichenin. Schulze, who reviewed the literature,[12] noted that most of the polysaccharides which yielded these other sugars were much more readily hydrolyzed than the remaining cellulose by aqueous acid and were extracted from the cell wall by aqueous alkali (cf. Payen's incrusting Fraction 1, Table 1). Schulze reserved the term cellulose for the constituent more resistant toward aqueous acid and freely soluble in cuprammonium. The less-resistant carbohydrates, constituted in the main from sugars other than glucose, were given the generic name of hemicelluloses. The differentiation, however, was not clean-cut because quite drastic extractions with acid and alkali failed to remove all of the hemicelluloses. Xylans and mannans, in particular, were partly but tenaciously retained by the cellulose residue. This circumstance prevented Schulze from claiming that cellulose invariably resembled cotton cellulose in containing nothing but glucose residues; indeed, three out of eleven different specimens gave hydrolyzates containing other sugars.

The noncellulose part of alcohol-ether-extracted plant tissue, called incrusting or ligneous matter by Payen, included, therefore, hemicelluloses as well as pectins.[9, 13] As the latter groups of substances were gradually recognized as distinct entities, the term lignin (Fremy's "vasculose"[14]) became restricted to denoting the noncarbohydrate fraction of the noncellulose incrustants[15, 16] (cf. Payen's Fractions 3 and 4, Table 1). This clarification in ideas and in nomenclature did much to explain the variation in staining reactions and general behavior that had led Fremy and others to deny the chemical uniformity of cellulose. Payen's argument assumed

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[11] R. Reiss, *Ber.*, **22**, 609 (1889).

[12] E. Schulze, *Ber.*, **24**, 2277 (1891); *Z. physiol. Chem.*, **16**, 387 (1892).

[13] B. Tollens, *Ann.*, **286**, 292 (1895).

[14] E. Fremy, *Compt. rend.*, **48**, 275 (1859); *J. pharm. chim.*, [3], **36**, 5 (1859).

[15] F. Schulze, *Jahresber. der Chem.*, **10**, 491 (1857); *Chem. Zentr.*, **1857**, 321.

[16] G. Dragendorff, *Die qualitative und quantitative Analyse von Pflanzen und Pflanzenteilen*. Vandenhöck and Ruprecht's Verlag, Göttingen, 1882, pp. 256–61. English translation by H. G. Greenish, Baillière, Tindall, and Cox, London, 1884, pp. 252–7. Dragendorff's separations and technique were surprisingly modern.

that the cellulose was isolated in a chemically unchanged form and the assumption was repeatedly supported by demonstrations that the cellulose[5, 12, 14, 17] and the lignin[12, 17] could be separately isolated as porous masses that retained the shape and detailed microscopic aspect of the original tissue. The latter was accordingly heterogeneous on the microscopic scale and it consequently could not be homogeneous on the molecular scale, as a uniform chemical combination between cellulose and incrusting substances demanded.

It was extremely unfortunate that many chemists failed to appreciate the force of the microscopic evidence and became unduly impressed with the regularities to be observed in the macroanalysis of cell-wall material. It had to be admitted that the isolation of cellulose frequently required the use of drastic chemical reagents, such as the nitric acid-potassium chlorate mixture introduced by Schulze,[15] and that cellulose itself was not always left unchanged by these reagents. With this background, it was plausible to argue that cellulose was an artifact produced by chemical change during isolation and to accept the varying physical properties of incrusted material, such as insolubility in cuprammonium, as evidence that the original tissue was a homogeneous chemical complex probably peculiar to each species of plant. Although earlier botanists, including Fremy, occasionally seemed to subscribe to this outlook, it first found full expression in the publications of Erdmann,[18] who considered the woody concretions sometimes found in pears to be "glycodrupose," $C_{24}H_{36}O_{16}$, while spruce wood was "glycolignose," $C_{30}H_{46}O_{21}$. Mild acid hydrolysis left "drupose," $C_{12}H_{20}O_8$, and "lignose," $C_{18}H_{26}O_{11}$, respectively, by the loss of reducing sugar. Subsequent extractions with dilute nitric acid progressively oxidized away an aromatic group related to catechol to leave a nearly constant over-all yield of wood fiber. Although Erdmann's views did not pass uncriticized,[19] they later received support from many quarters and particularly from Cross and Bevan. These authors claimed that jute and other bast fibers were uniform in elementary composition, chemical reactions, staining behavior, and microscopic appearance along their length. The residue obtained after partial solution gave the same analytical figures, and the fibrous structure was retained during oxidation, chlorination, acid hydrolysis, and treatments

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[17] J. König and E. Rump, *Chemie und Struktur der Pflanzen-Zellmembran*. pp. 85–88, plates 1–7; see ref. 2, p. 29.

[18] J. Erdmann, *Ann.*, 5, supplementary binding, 223 (1867).

[19] R. Sachsse, *Die Chemie und Physiologie der Farbstoffe, Kohlenhydrate und Proteinsubstanzen*. L. Voss, Leipzig, 1877, pp. 150–52.

with aqueous sodium sulfite.[20] On this basis, jute was "bastose," or $C_{76}H_{80}O_{37}$,[21] while related names and formulas were given to derived products. Cross and Bevan believed that in the plant the cellulose, pectin, lignin, and fatty material merged into one another by insensible chemical gradations and they called the original complexes "ligno-," "pecto- or muco-," "adipo- or cuto-cellulose" according to the constituents preponderating in a given fiber. "Cellulose" was merely the aggregate resulting from a chemical breakdown carried to the point where the reactions generally accepted for pure cellulose were obtained. This view, indefatigably upheld and amplified,[20, 22] had many adherents during the period 1880 to 1920.

Although the lignocellulose theory was never much more than a reversion to a pre-Payen outlook, its protagonists were obviously not to be convinced of its inadequacy by any evidence that involved the use of chemicals. Rebuttal came through physical studies on the birefringence and swelling of cellulose fibers by Nägeli, Ambronn, and their successors and by the development of x-ray technique (Chapter III). These studies gradually built up an overwhelming case for the modern concept of fibrous cellulose as being an essentially crystalline body, shot through and through with submicroscopic faults and disorganized localities. It was incredible that a uniform, regularly organized crystal lattice could be in uniform chemical combination throughout its bulk with large, amorphous molecules of lignin, fat, or hemicellulose substances. The gradual abandonment of the lignocellulose theory may be dated from 1920, when Herzog and Jancke showed that lignified fibers, jute and lime (linden) wood, gave practically the same x-ray pattern as delignified wood pulp or as flax, ramie, or cotton.[23] Recent microdissections of woods[24] and recent x-ray studies on the submicroscopic porous structure of cellulose[25] showed beyond doubt that the incrustants tend to be concentrated in the capillaries and between individual cells.

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[20] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **38**, 666 (1880); **41**, 90 (1882); **43**, 18 (1883); **55**, 199 (1889); *Cellulose.* 1st ed., 1895; 2nd ed., 1903; 3rd ed., 1916; *Researches on Cellulose, 1895–1900; 1900–1905; 1905-1910.* Longmans, Green & Co., London.

[21] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **55**, 199 (1889).

[22] C. F. Cross and C. Dorée, *Researches on Cellulose, 1910–1921.* Longmans, Green & Co., London, 1922.

[23] R. O. Herzog and W. Jancke, *Ber.*, **53B**, 2162 (1920).

[24] A. J. Bailey, *Ind. Eng. Chem., Anal. Ed.*, **8**, 52, 389 (1936).

[25] A. Frey-Wyssling, *Protoplasma*, **25**, 261 (1936). This article contains an excellent discussion of the earlier literature.

This modern conclusion is entirely in line with a theory of incrustation enunciated by H. Wislicenus in 1910.[26] The early spring sap of various trees was treated with filter paper or alumina gel and only 4 to 8% of the total solids was adsorbed from solution. The adsorbed material was assumed to represent the colloidal, as opposed to the crystalloidal, contents of the sap. Cambial sap, isolated at the height of the growing season, contained up to 37%, but when growth stopped in the late summer the amount fell sharply to 6 to 8%. Incrustation was therefore regarded as a physical process in which the sap colloids coagulated or were adsorbed upon the enormous internal surface of a previously elaborated, highly porous cellulose framework. The question as to whether or not a few main valence bonds establish themselves between the cellulose surface and the adsorbed incrustants is discussed in Section E of this chapter.

Although the general acceptance of the micellar theory now renders the concept of lignocellulose, together with the associated nomenclature, quite obsolete, the historical controversies about a proper definition of cellulose have not yet been entirely resolved. The fibrous, delignified pulps isolated by one procedure or another, as by the alternating chlorination-sodium sulfite extractions of Cross and Bevan,[27] are still often named celluloses, especially in textile and botanical circles. On this basis, cellulose is the natural, fibrous, carbohydrate, structural aggregate of the cell wall[28, 29] and usually includes a hemicellulose fraction yielding sugars other than glucose on acid hydrolysis. Cotton cellulose, consisting entirely of glucose residues, is thus an abnormal type.[28] The alternative definition follows Payen and Schulze in accepting cotton as a standard and consequently restricts the term cellulose to that portion of the cell wall derived exclusively from glucose and resembling cotton cellulose in its physical and chemical properties. This definition has been openly or tacitly adopted by the great majority of those interested mainly in studies of chemical structure, which almost invariably have been carried out with cotton or filter paper.

While it is true that the deeper insight of today enables a careful author to oscillate between the two definitions and yet remain intelligible, the double standard created great confusion in the past. In the interests of

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[26] H. Wislicenus, *Kolloid-Z.*, **6**, 87 (1910); **27**, 209 (1920).

[27] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **38**, 667 (1880).

[28] A. G. Norman, *The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.* Clarendon Press, Oxford, 1937, pp. 1–4.

[29] J. T. Marsh and F. C. Wood, *An Introduction to the Chemistry of Cellulose.* Chapman & Hall, London, 1938, p. 1.

clarity as well as in deference to the brilliant pioneering of Payen, the writer intends to use the unmodified term cellulose in Payen's sense and to denote as pulps all aggregates known to contain hemicellulose fractions. Particular aggregates, of course, may also be very properly described by qualifying the word cellulose as, for example, alpha-cellulose, or Cross and Bevan cellulose.

2. Discoveries of Industrial and Theoretical Interest

In addition to the rather botanical lines of research just described, the nineteenth century witnessed several disconnected developments which became of great technical importance. Payen's use of strong, hot alkali and of chlorine for pulping woods and grasses led, in the 1860's, to the establishment of the kraft and sulfate industries[30] while the sulfite process was first described by Tilghman, of Philadelphia.[31] Schwalbe's textbook gives a more detailed, tabular review of progress in this field.[32]

The self-taught English chemist Mercer made many contributions to the technique of dyeing and printing calico in the period 1840 to 1860 but his discoveries were not generally known until a later date.[33, 34] About 1844, he carefully studied the action of cold, strong caustic soda on cotton yarn and noted the shrinkage in dimensions, and the increase in strength, in affinity for dyes, and in the weight of the washed and air-dried product[35] (mercerized yarn). The process was interpreted as involving an intermediate alkali cellulose complex $(C_6H_{10}O_5)_2 \cdot Na_2O$, and as giving a cellulose hydrate $(C_6H_{10}O_5)_2 \cdot H_2O$. Mercer's patent on this process (1850) also in-

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[30] A. Mellier, patented in France in 1854 and applied to woods about 1865. Quoted from Hess, *Die Chemie der Zellulose*, p. 244; see ref. 1, p. 29.

[31] B. C. Tilghman, abstracts in *Bull. soc. chim.*, [2], **8**, 137 (1867); *Ann. génie civil*, p. 271 (Apr., 1867); *Jahresber. der Chem.*, **20**, 952 (1867). See also A. Mitscherlich, *Jahresber. der Chem.*, **1876**, 1172; *Dinglers Polytech. J.*, **220**, 479, 564 (1876); and W. B. Wheelwright, *Paper Makers J.* (U. S.), **39**, 20 (1940).

[32] C. G. Schwalbe, *Die Chemie der Cellulose*. Gebrüder Borntträger, Berlin, 1911, p. 509.

[33] Obituary in *J. Chem. Soc.*, **20**, 395 (1867).

[34] E. A. Parnell, *The Life and Labours of John Mercer*. Longmans, Green & Co., London, 1886, pp. 175–207, 214–16, 317.

[35] The question of priority is discussed by the editors of *The Dyer and Calico Printer* in *Mercerization. A Practical and Historical Manual*. Vol. I, Heywood and Co., London, 1903, pp. 1–10. A. Wurtz, *Dictionnaire de Chemie*, Vol. I, Hachette and Co., Paris, 1876, p. 779, attributes the discovery of mercerization to Persoz. Girard (ref. 58, p. 38) states that the initial publication was by Persoz in 1846. See also Schwalbe, *Die Chemie der Cellulose*, p. 37; see ref. 32, above.

cluded the parchmentizing effect of strong sulfuric acid[36, 37] and zinc chloride solutions on paper and yarn. Mercer, in addition, gave a detailed description of the solubility of cotton in strong cuprammonium solution[38] and of the regeneration of the cellulose on the addition of acid. These observations led in time to the large-scale production of cellulose xanthates (viscose) and benzoates.[39] Leuchs,[40] Lilienfeld,[41] and Denham and Woodhouse[42] independently but almost simultaneously used alkali cellulose and an alkyl halide[43] or sulfate to prepare the alkylated derivatives. The cuprammonium rayon industry, however, probably originated with the independent duplication of Mercer's observations by Schweizer[44] and their amplification by Cramer[45] and Schlossberger.[46]

In 1833, Braconnot, following up an observation of Pelouze, showed that pure, anhydrous nitric acid differed from the dilute acid in having little effect on insoluble alkali and alkaline earth carbonates. Braconnot was led to try the action of the anhydrous acid on various polysaccharides, including cotton, linen, and wood shavings. The highly flammable, neutral powders (xyloidins) dissolved in concentrated acetic acid and the solutions deposited tough, varnish-like films as clear as glass.[47] The somewhat more highly nitrated guncottons were independently discovered by Böttger[48] and by Schönbein[49] who obtained products of technical value by using concentrated sulfuric acid as a catalyst in the nitration. It is inter-

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[36] J. A. Poumarède and L. Figuier, *J. pharm. chim.*, **11**, 81 (1847); *J. prakt. Chem.*, **42**, 25 (1847).

[37] C. E. Guignet, *Compt. rend.*, **108**, 1258 (1889). This type of parchmentized cellulose was frequently called "Guignet cellulose."

[38] Quoted from C. F. Cross and E. J. Bevan, *Cellulose*, 1st ed., p. 13; see ref. 20, p. 34.

[39] C. F. Cross, E. J. Bevan, and C. Beadle, *Ber.*, **26**, 1090 (1893).

[40] O. Leuchs, German Patent 322,586 (Jan. 26, 1912). Quoted from Hess, *Die Chemie der Zellulose*, p. 429; see ref. 1, p. 29.

[41] L. Lilienfeld, Brit. Patent 12,854 (May 31, 1912); *Chem. Abstracts*, **7**, 3839 (1913).

[42] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **103**, 1735 (1913).

[43] M. Berthelot, *Ann. chim. phys.*, [3], **60**, 103 (1860), probably obtained a crude, partly alkylated sucrose by heating the sugar with a mixture of potassium hydroxide and ethyl bromide.

[44] E. Schweizer, *J. prakt. Chem.*, **72**, 109 (1857).

[45] C. Cramer, *J. prakt. Chem.*, **73**, 1 (1858).

[46] J. E. Schlossberger, *J. prakt. Chem.*, **73**, 371 (1858).

[47] H. Braconnot, *Ann.*, **7**, 242, 245 (1833). An addendum by J. Liebig notes that Braconnot's products contained nitrogen and detonated weakly on heating.

[48] C. F. Schönbein and R. Böttger, *Poggendorff's Ann. der Physik und Chemie*, **70**, 320 (1847).

[49] C. F. Schönbein, *Phil. Mag.*, **31**, 7 (1847).

esting to note that by 1847 the most highly nitrated cellulose nitrate was correctly recognized as one in which three molecules of water per glucose residue had been replaced by the elements of three molecules of nitric acid,[50, 51] and that the partial denitration of guncotton to pyroxylin in dilute nitric acid led Gladstone to suggest that the nitration reaction was an equilibrium.[52] Schützenberger, who acetylated cellulose with hot acetic anhydride, was also prompt to recognize that the most highly substituted acetate was a triacetate.[53] He was not interested in the analyses of lower acetates owing to the probability that they were mixtures containing unchanged cellulose. The use of concentrated sulfuric acid or zinc chloride as a catalyst in the acetylation was introduced by Franchimont, who noted that the progressive increase in the crystallinity of the products obtained with various conditions paralleled the decrease in molecular complexity toward that of acetylated glucose.[54] This research unearthed the crystalline octaacetate of the reducing disaccharide cellobiose,[55] although an analytical error caused Franchimont to consider it as a fully acetylated trisaccharide. Cross and Bevan[56] studied the preparation of cellulose triacetate, and a method of partial deacetylation introduced by Miles[57] opened the way to modern, acetone-soluble derivatives.

The cause of the "tendering" of fabrics during bleaching with hypochlorite and during other textile operations remained an enigma until the period 1880–83, when Girard, and especially Witz. published researches on the subject which still merit detailed study. Girard showed that acids of any sort, organic, inorganic, strong or weak, in dilute or concentrated aqueous solution, in the gaseous state or dried into the cloth, invariably reduced the tensile strength to zero and yielded a water-insoluble friable powder. When the latter was suitably dried *in vacuo*, it invariably had a composition close to that of $(C_6H_{10}O_5)_2 \cdot H_2O$ and Girard accordingly named it hydrocellulose.[58] The notable research of Witz started with the observa-

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[50] Some contemporaneous analyses were discordant. See reviews in *Ann.*, **64**, 391 (1847) and *Jahresber. der Chem.*, **1**, 1128 (1847–48).

[51] W. Crum, *Ann.*, **62**, 233 (1847); *Phil. Mag.*, **30**, 426 (1847).

[52] J. H. Gladstone, *Phil. Mag.*, **31**, 519 (1847).

[53] P. Schützenberger, *Ann. chim. phys.*, [4], **21**, 235 (1870).

[54] A. P. N. Franchimont, *Ber.*, **12**, 1938 (1879); *Rec. trav. chim.*, **18**, 472 (1899).

[55] Z. H. Skraup, *Ber.*, **32**, 2413 (1899).

[56] C. F. Cross and E. J. Bevan, *Cellulose*, 1st ed., p. 38; see ref. 20, p. 34. These authors considered for years that the most highly substituted cellulose acetate contained four acetyl groups for each glucose residue.

[57] G. W. Miles, U. S. Patent 838,350 (Dec. 11, 1906); *Chem. Abstracts*, **1**, 653 (1907).

[58] A. Girard, *Ann. chim. phys.*, [5], **24**, 337 (1881).

ion that certain bleached cottons contained many minute holes, the edges of which discolored on gentle heating and adsorbed certain dyestuffs intensely. Witz proved that such damage was due to the adventitious adherence of solid calcium hypochlorite dust to the moist fabric.[59] A clever use of dyestuffs then enabled him to eliminate local acidity, leading to hydrocellulose, as a cause of the damage, while elementary analyses showed that the hypochlorite functioned not as a chlorinating but as an oxidizing agent. The friable, overbleached calico was accordingly named oxycellulose.[60] Increased affinity for methylene blue and many other dyestuffs, increased copper-reducing power, and decreased mechanical strength then formed criteria by means of which Witz was able to classify as oxidations other phenomena which troubled the textile trade. These oxidations included catalytic effects such as those with sunlight and air; sunlight, air, and iron salts; alkali and air; vanadium and chlorates; as well as more obvious ones with permanganates and dichromates in solutions of varying acidity.

Concurrently with the above work, structural organic chemistry in general was being built up with brilliant success by arguments based on the analyses of substances which were chemical individuals. But cellulose and its derivatives were generally fibrous, insoluble materials which had no sharp melting or boiling points and which gave negative or indefinite results in molecular-weight determinations. Deprived of the usual criteria of homogeneity and purity, investigators in the cellulose field very frequently made the mistake of assuming these qualities in their preparations on insufficient evidence and accordingly attached molecular meanings to their analytical data. As the composition of mixtures naturally varied with the details of the individual preparation, a confusion of divergent formulas was applied to products obtained by essentially the same means, and the originator of each formula insisted on exact adherence to a special set of conditions. The varying percentage of water in hydrocellulose led to formulas ranging from $(C_6H_{10}O_5)_2 \cdot H_2O$ to $(C_6H_{10}O_5)_6 \cdot H_2O$,[61, 62, 63] until

[59] G. Witz, *Bull. soc. ind. Rouen*, **11**, 169 (1883); **12**, 638 (1883). Extensive abstract in *Dinglers Polytech. J.*, **250**, 271 (1883).

[60] Witz restricted the term to material preserving the physical appearance and insolubility of the original fibers and called the more highly reducing, alkali-soluble byproduct of the oxidations "celluloglucose." The latter corresponded in properties to the nitric acid oxycellulose described a few months later by Cross and Bevan, *J. Chem. Soc.*, **43**, 22 (1883).

[61] C. G. Schwalbe, *Z. angew. Chem.*, **20**, 2166 (1907).

[62] H. Ost, *Z. angew. Chem.*, **19**, 993 (1906).

[63] G. Büttner and J. Neuman, *Z. angew. Chem.*, **21**, 2609 (1908).

it was shown that proper washing and thorough drying resulted in the empirical formula $C_6H_{10}O_5$.[64, 65] The latter composition was eventually adopted for regenerated cellulose (viscose) and for Mercer's cellulose hydrate,[66] which differed from hydrocellulose in having a much smaller copper-reducing power.[61] Although Franchimont's acetylation studies quickly made him suspect that Witz's original oxycellulose specimens contained much unchanged cellulose,[67] it became customary for years to attach empirical formulas to oxycelluloses prepared by different methods.[68] The extensive work of Berl and Klaye did much to demonstrate the irreproducibility of the analytical data.[69] Hess showed that oxycelluloses had substantially the same optical rotation in cuprammonium as cellulose itself[70] and the more general studies of Hibbert and Parsons[71] and Heuser and Stöckigt[72] demonstrated the heterogeneous nature of the oxidations.[71, 73]

Structural ideas concerning the esters of cellulose underwent analogous modifications. Attempts to represent the lower nitrates by formulas varying from $C_{24}H_{36}O_{16}(NO_3)_4$ to $C_{24}H_{28}O_8(NO_3)_{12}$,[74] or even by similar formulas based on a C_{48} unit.[75] were gradually abandoned with the recognition that the nitration reaction was an equilibrium governed by the amount of water in the spent nitrating liquor[51, 69] and complicated by the formation of hydro- and oxy-cellulose nitrates.[69] Similar complications, together with uncertainty about the reliability of acetyl analyses, delayed the general acceptance of the triacetyl, rather than the tetraacetyl,[56] derivative as the most highly substituted cellulose acetate until 1906.[53, 76] Representations

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[64] A. L. Stern, *J. Chem. Soc.*, **85**, 336 (1904).

[65] H. Ost, *Ann.*, **398**, 313 (1913).

[66] H. Ost and F. Westhoff, *Chem.-Ztg.*, **33**, 197 (1909).

[67] A. P. N. Franchimont, *Rec. trav. chim.*, **2**, 241 (1883).

[68] C. G. Schwalbe, *Die Chemie der Cellulose*, pp 129–44, 160–262 (see ref. 32, p. 36), gives an extensive account of early hydrocellulose, cellulose hydrate, and oxycellulose researches.

[69] E. Berl and R. Klaye, *Z. ges. Schiess- u. Sprengstoffw.*, **2**, 381, 403 (1907); *Chem. Abstracts*, **2**, 184, 898 (1908).

[70] K. Hess, *Z. angew. Chem.*, **37**, 993 (1924).

[71] H. Hibbert and J. L. Parsons, *J. Soc. Chem. Ind.*, **44**, 473T (1925). This article contains an excellent review of the literature.

[72] E. Heuser and F. Stöckigt, *Cellulosechem.*, **3**, 61 (1922).

[73] P. H. Clifford and R. G. Fargher, *Shirley Inst. Mem.*, **1**, 118 (1922); *J. Textile Inst.*, **13**, T189 (1922). A comprehensive review.

[74] J. M. Eder, *Ber.*, **13**, 169 (1880). A table of earlier formulas is included.

[75] D. I. Mendeleev, *Mon. sci.*, p. 510 (1897); quoted by G. Lunge and J. Bebié, *Z. angew. Chem.*, **14**, 483 (1901).

[76] H. Ost, *Z. angew. Chem.*, **19**, 993 (1906).

of the sulfuric acid ester salts as $C_{10}H_{20}O_2(SO_3)_2 \cdot BaO \cdot 2H_2O$ [77] and analogous formulas were later shown to have no validity.[78] Finally, in 1936, the variable composition of the xanthate esters was fully recognized by Lieser and Leckzyck.[79]

Although the enormous mass of research so briefly catalogued above was in many respects of permanent value to industry, the data as a whole served to confuse rather than clarify the structural chemistry of cellulose. The truth of this statement is seen in the diversity of formulas suggested for cellulose and by the hesitation with which each suggestion was advanced by its sponsors. The merits and demerits of the following proposals have been carefully discussed by Hibbert.[80]

Structures II and III were considered to explain the 26% yield of ω-bromofurfuraldehyde obtained from cellulose by hydrogen bromide in chloroform.[81] Cross and Bevan formulas such as II were also unique in their claims that the hexose unit in cellulose was more closely related to a keto sugar than to glucose and that these units contained four, rather than three, hydroxyl groups capable of being acetylated. Various modifications of the tannin-like model VI ("celluxose") assumed 3.3 to 3.1 hydroxyl groups, gave special consideration to the yields of cellobiose octaacetate recovered in the acetolysis of cellulose, and recognized that the glucoside linkage was very common in nature. Barthelemy's more complicated unit V contained ethylene oxide rings which were supposed to add on the elements of caustic soda during the preparation of alkali cellulose. A similar argument, together with the existence of cellobiose, had led Vieweg[82] to another anhydrodisaccharide ($C_{12}H_{20}O_{10}$) structure, polymerized in an unknown way. The composition of various cellulose nitrates also made Eder favor much the same conclusion.[83] Vignon (Structure I) was particularly interested in the reactions of oxycellulose while Pictet and his collaborators later supported the same formula because crystalline β-glucosan (I, $n = 1$) was produced by distilling starch destructively at 210°C. at 10 mm.[84] All authori-

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[77] M. Hönig and S. Schubert, *Monatsh.*, **6**, 708 (1885). These authors recognized that the cellulose was degraded.

[78] A. L. Stern, *J. Chem. Soc.*, **67**, 74 (1895). A good review is included.

[79] T. Lieser and E. Leckzyck, *Ann.*, **522**, 56 (1936).

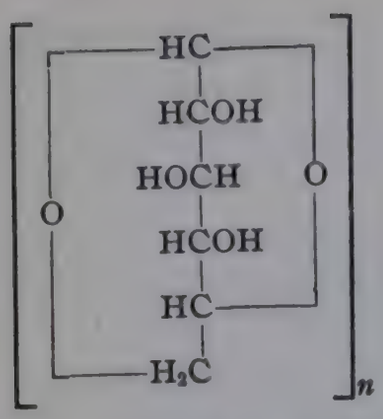
[80] H. Hibbert, *Ind. Eng. Chem.*, **13**, 256, 334 (1921).

[81] H. J. Fenton and M. Gostling, *J. Chem. Soc.*, **79**, 361 (1901).

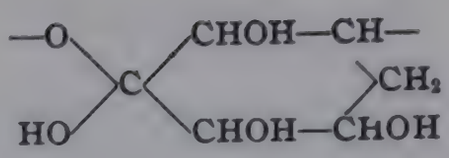
[82] W. Vieweg, *Ber.*, **40**, 3876 (1907).

[83] J. M. Eder, *Ber.*, **13**, 176 (1880).

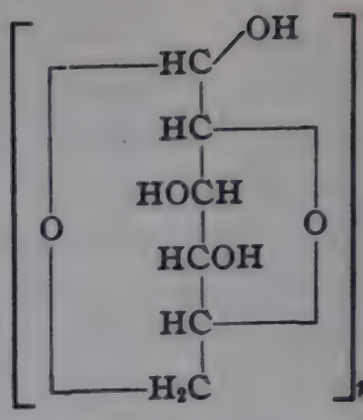
[84] Formula I was conclusively disproved by J. C. Irvine and J. W. Oldham (*J. Chem. Soc.*, **119**, 1744 (1921); **127**, 2903 (1925)) who methylated β-glucosan and dextrins derived from it by heating with zinc chloride.



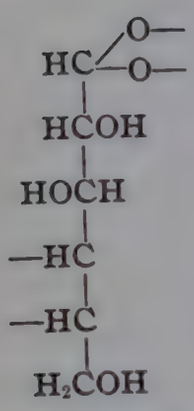
I. Vignon,[85] Pictet[86, 87, 88]



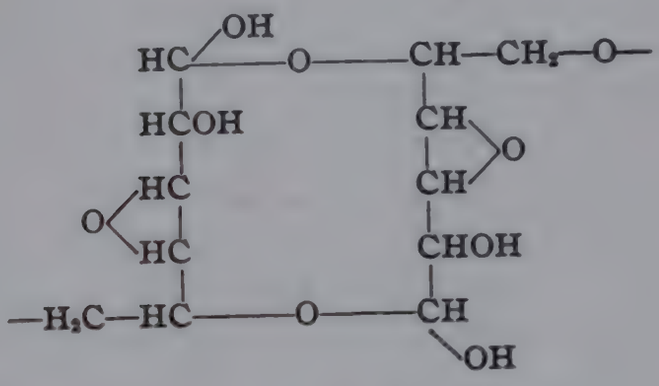
II. Cross and Bevan[89]



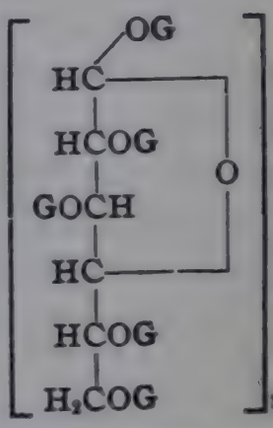
III. Green[90, 91]



IV. Tollens[92]



V Barthelemy[93]



(G is a glucosyl group

VI. Hess[94]

SOME EARLY FORMULAS PROPOSED FOR CELLULOSE

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[85] L. Vignon, *Bull. soc. chim.*, [3], **22**, 597 (1899).

[86] A. Pictet and J. Sarasin, *Helv. Chim. Acta*, **1**, 87 (1918).

[87] A. Pictet and M. Cramer, *Helv. Chim. Acta*, **3**, 640 (1920).

[88] A. Pictet and J. H. Ross, *Helv. Chim. Acta*, **5**, 876 (1922).

[89] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **79**, 366 (1901). See also *Researches o* *Cellulose, 1895–1900*, p. 77; *1900–1905*, p. 102; and *Cellulose*, 1st ed., p. 75; see ref. 20 p. 34.

[90] A. G. Green, *Z. Farben- u. Textilchem.*, **3**, 97 (1904).

[91] A. G. Green and A. G. Perkin, *J. Chem. Soc.*, **89**, 811 (1906).

[92] B. Tollens, *Kurzes Handbuch der Kohlenhydrate*. Vol. 2, E. Trewendt, Breslau 1895, p. 252.

[93] H. Barthelemy, *Caoutchouc & gutta-percha*, **14**, 9274 (1917); *Chem. Abstracts*, **11** 3428 (1917).

[94] K. Hess and W. Wittelsbach, *Z. Elektrochem.*, **26**, 232 (1920); K. Hess, *Hel* *Chim. Acta*, **3**, 866 (1920).

ties recognized that the physical properties of cellulose and its solutions indicated a molecular weight far greater than that of a single glucose residue. Formulas II, IV, and V expressed this fact by conventional main valence linkages of a type that was broken by acid hydrolysis. Formulas I, III, and VI, on the other hand, were self-contained from the main valence point of view and their originators attributed the high molecular weight of cellulose to "association" between secondary valence forces analogous to those holding individual atoms of silver in place in the colloidal particle,[94] or to "physical aggregates" such as are constantly found occurring in the case of colloidal substances.[91] This tendency to stress the colloidal aspect of cellulose was occasionally carried to the point of denying that the methods of classical organic chemistry would ever assign a definite structure to the polysaccharide.[95]

On looking backward through the decades from the vantage point of the present, it is easy to see that the structural chemistry of cellulose remained at a virtual standstill from 1860 to 1920 because ancillary sciences, indispensable to a solution of the problem, were in an undeveloped condition. By 1920, the labors of Emil Fischer and other investigators had placed the chemistry of the simple sugars upon a solid foundation.[96] The methylation method of determining the position of hydroxyl groups in the carbon skeleton completed its long apprenticeship, in the hands of Purdie, Irvine, Denham and Woodhouse, and others, about the same time, and the essential, partly methylated glucoses had been prepared and characterized.[97] X-rays gave the first clear diffraction pattern of fibrous cellulose in 1920[23] and shortly thereafter the colloid chemistry of linear macromolecules, such as cellulose proved to be, was very greatly clarified by Staudinger and his collaborators.[98] These events make it convenient to choose the year 1919, when Emil Fischer died, as the beginning of the modern period of cellulose chemistry.

3. Rise and Decline of the Association Theory

Much of the doubt surrounding the structure of cellulose was swept away at one stroke when almost completely methylated cotton was degraded in very good yield to the well-characterized, crystalline 2,3,6-trimethylglu-

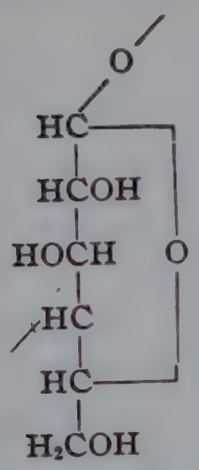
[95] C. F. Cross and E. J. Bevan, *Researches on Cellulose, 1900–1905*, pp. 1–7; see ref. 20, p. 34.

[96] C. S. Hudson, *J. Chem. Education*, **18**, 353 (1941).

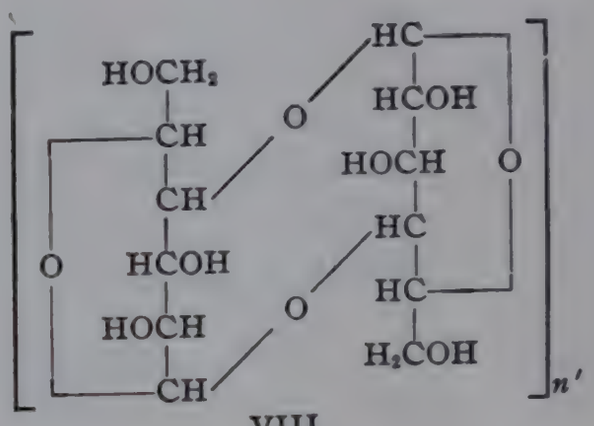
[97] J. C. Irvine, *J. Chem. Soc.*, **123**, 898 (1923).

[98] H. Staudinger, *Die hochmolekularen organischen Verbindungen*. J. Springer, Berlin, 1932.

cose.[99, 100] This result demonstrated that hydroxyl groups occupied the second, third, and sixth positions of each glucose residue in cellulose. All of the older formulas for the polysaccharide were invalidated except a suggestion of Hibbert's (Structure VII) which was based on preliminary methylation data and in part upon the relative ease of formation and conversion displayed by five- and six-membered cyclic acetals.[80] The adoption of the pyran ring structure for the more stable type of glucosides,[101, 102] together with the demonstration that cellobiose was a 4-glucopyranosylglucose,[103, 104] then made it reasonable to regard cellulose as a linear macromolecule[105, 106, 107] in which uniform and equivalent, main valence glucosidic links unite a large number of hexose units (Structure VII).



VII (repeat n times)



VIII

This view is almost universally accepted today and all other sections of this text are devoted to expounding it. The point of immediate interest is that in the early 1920's the proponents of Formula VII were unable to adduce convincing proof in its support. Their failure in this respect permitted an alternative interpretation of the facts to gain much ground and to stimulate a large volume of research.

The physical properties of fibrous cellulose and of its solutions had

[99] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **123**, 518 (1923).

[100] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **103**, 1735 (1913); **105**, 2357 (1914).

[101] E. L. Hirst, *J. Chem. Soc.*, **1926**, 350.

[102] W. Charlton, W. N. Haworth, and S. Peat, *J. Chem. Soc.*, **1926**, 89.

[103] G. Zemplén, *Ber.*, **59B**, 1254 (1926).

[104] W. N. Haworth, C. W. Long, and J. H. G. Plant, *J. Chem. Soc.*, **1927**, 2809.

[105] This name was coined by H. Staudinger and J. Fritschi, *Helv. Chim. Acta*, **5**, 785 (1922).

[106] H. Staudinger, *Ber.*, **53B**, 1081 (1920).

[107] K. Freudenberg, *Ber.*, **54B**, 767 (1921).

created a deep-seated feeling that the polysaccharide was essentially a colloidal substance.[108] Unfortunately for the study of cellulose and other high polymers, most of the spectacular early successes of colloid chemistry did not concern linear macromolecules but were obtained with atoms or small molecules which assembled in regular array to form aggregates of colloidal size. The forces responsible for such aggregation were clearly of the residual or secondary valence type active in the molecular lattice of a crystal or between the molecules of a fatty acid associated in a nonpolar solvent like benzene. These suspensoid, association, or micellar[109] colloids included aqueous sols of many metals, of dyestuffs like indigo, and of soaps in the sol, gel, and curd form. The micellar structure of the soaps was the subject of particularly intensive studies by McBain and his collaborators.[110, 111] These systems resembled solutions of cellulose and its derivatives in the unexpectedly minute values they displayed in osmotic pressure and similar determinations, in their abnormal viscosity phenomena, and in the erratic and apparently capricious way the quantitative data depended on the previous history of the specimen and on the experimental details. *A priori*, it was indeed reasonable to argue, as Vignon, Green, and Hess had done (Structures I, III, and VI), that cellulose was similarly constituted. Only a few glucose units were assumed to be united by main valences to give a $(C_6H_{10}O_5)_x$ molecule, large numbers, n', of which then associated to a physical aggregate whose average size was greatly dependent on the physicochemical environment. Formula VIII represents the case in which x is two and the true chemical molecule is chosen to satisfy the methylation data. Although the nature of the forces holding such main valence molecules in aggregates always remained obscure, it was supposed that they resembled those responsible for soap micelles or for the coordination complexes so convincingly explained by Werner.[112, 113, 114] The word "polymerization" lost its precision for a few years because some writers extended its meaning to include the concept of "association" or "aggrega-

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[108] C. G. Schwalbe, *Die Chemie der Cellulose*, p. 356, (see ref. 32, p. 36) reviewed the earlier work.

[109] "Micelles" were originally the submicroscopic crystallites whose presence in fibrous cellulose was inferred by Nägeli.

[110] M. E. Laing and J. W. McBain, *J. Chem. Soc.*, **117**, 1506 (1920).

[111] J. W. McBain, *J. Phys. Chem.*, **30**, 239 (1926).

[112] A. Werner, obituary, *J. Chem. Soc.*, **117**, 1639 (1920). Biography by P. Peiffer, *J. Chem. Education*, **5**, 1090 (1928).

[113] N. V. Sidgwick, Presidential Address, Section B, *Brit. Assoc. for the Advancement of Science Reports*. Spottiswoode Ballantyne & Co., London, 1927, p. 27.

[114] M. Bergmann, *Ber.*, **59B**, 2973 (1926).

tion"[115, 116] while others did not.[98, 117] In the same way, "molecular weight" was not infrequently confused with "particle" or "micellar" weight.[118]

The association theory also appeared to be supported by experimental evidence in other fields, for it was known that the destructive distillation of rubber yielded isoprene and that isoprene, with suitable catalysts, gave back a rubber-like material. Starch, too, was changed by *Bacillus macerans* to a mixture of the Schardinger dextrins, which were nonreducing, crystalline substances with apparent molecular weights of from two to eight anhydroglucose units,[119, 120] but now known to contain six or seven such units in a ring.[121] When applied to cellulose, the theory not only provided plausible although *ad hoc* explanations of the physical properties of the solutions but was compatible with x-ray and optical data obtained from the solid fiber (see Chapter III). These data indicated that much of the fiber consisted of crystallites or micelles of colloidal dimensions and that each x-ray unit cell contained only a small number of glucose residues.[122, 123, 124] While Structure VII had to be of great length in order to explain the experimental failure to find units corresponding to the ends, Structure VIII required no additional assumptions in this respect. Supported by this series of arguments, many chemists came to believe that suitable solvents or chemical reagents might "depolymerize" cellulose to small, main valence molecules of a kind which would readily revert to aggregates of colloidal size. Several well-known textbooks were written from this point of view.[1, 115, 116] It is now necessary to record some of the fruitless attempts that were made to support these ideas experimentally.

The first emphatic rejections of the macromolecular theory came from Hess and from Karrer. Karrer and his collaborators determined the heats of combustion of several compound sugars, $(C_6H_{10}O_5)_n \cdot H_2O$, where n was

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[115] See, for example, H. Pringsheim, *The Chemistry of the Monosaccharides and of the Polysaccharides*. McGraw-Hill, New York, 1932.

[116] See for example, P. Karrer, *Polymere Kohlenhydrate*. Akademische Verlagsgesellschaft m. b. H., Leipzig, 1925.

[117] See, for example, K. Hess, *Die Chemie der Zellulose*, p. 576; see ref. 1, p. 29.

[118] The colloidal aspects of the macromolecular and association theories were ably reviewed by H. Staudinger, *Kolloid-Z.*, **53**, 19 (1930). See also H. Staudinger, K. Frey, R. Signer, W. Starck, and G. Widmer, *Ber.*, **63B**, 2308 (1930).

[119] H. Pringsheim and F. Eissler, *Ber.*, **46**, 2959 (1913).

[120] P. Karrer and C. Nägeli, *Helv. Chim. Acta*, **4**, 169 (1921).

[121] D. French and R. E. Rundle, *J. Am. Chem. Soc.*, **64**, 1651 (1942).

[122] K. H. Meyer and H. Mark, *Ber.*, **61B**, 593 (1928).

[123] H. Mark, *Ber.*, **59B**, 2982 (1926), reviewed the earlier x-ray results.

[124] M. Polanyi, *Naturwissenschaften*, **9**, 337 (1921).

2 to 4, and noted that the values increased to that of β-glucosan, $C_6H_{10}O_5$. Starch, various crystalline starch dextrins, and cellulose had the same heat of combustion as β-glucosan. This result indicated either that n' was unity in Structure VIII or that the Chain VII contained a large number of units (more than sixty). The latter alternative was rejected as highly improbable and the association hypothesis was considered to have received decisive support.[125, 126] A little previously, Hess and his collaborators had discovered that the specific rotation of cellulose dissolved in a caustic soda-cuprammonium solution reached a maximum when one atom of copper was present for each glucose residue. This rotation was independent of the origin of the cellulose, provided no other polysaccharide was present, and was also independent of the concentration, provided the latter was above a certain minimum value. A glucosan structure was assumed for cellulose because, in this event, the formation of the copper complex obeyed the mass action law. The fact that the data were also consistent with a sufficiently long chain of anhydroglucose units seems to have been ignored.[127] Traube,[128] as well as Neale,[129] also discussed the supposed constitution of the cellulose-copper-alkali complex in detail.

Hess and his collaborators were very successful in obtaining ramie cellulose,[130] cellulose triacetate,[131] trimethyl- and triethyl-cellulose,[132, 133] and an acetone-cellulose nitrate complex[134] in crystalline form. In each case some acidic pretreatment was involved, and today the formation of such micro or semimicro, rather soft crystals is recognized as a typical characteristic of linear macromolecules of intermediate chain length.[135] The phenomenon, however, was claimed by Hess as evidence for the simple anhydroglucose Structure VIII on the ground that colloidal aggregates were not likely to crystallize.

Another argument for the association theory was found in the physical behavior of dilute solutions of cellulose and its derivatives in glacial acetic

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[125] P. Karrer, C. Nägeli, O. Hurwitz, and A. Wälti, *Helv. Chim. Acta*, **4**, 678 (1921).
[126] P. Karrer, *Ber.*, **55B**, 2854 (1922).
[127] K. Hess, W. Weltzien, and E. Messmer, *Ann.*, **435**, 1 (1924).
[128] W. Traube, *Ber.*, **54B**, 3220 (1921); **55B**, 1899 (1922); **56B**, 268, 1653 (1923).
[129] S. M. Neale, *J. Textile Inst.*, **16**, T363 (1925).
[130] K. Hess and G. Schultze, *Ann.*, **456**, 55 (1927).
[131] K. Hess, G. Schultze, and E. Messmer, *Ann.*, **444**, 266 (1925); K. Hess, *Z. angew. Chem.*, **37**, 999 (1924).
[132] K. Hess and H. Pichlmayr, *Ann.*, **450**, 29 (1926).
[133] K. Hess and A. Müller, *Ann.*, **455**, 205 (1927).
[134] K. Hess, C. Trogus, and K. Dziengel, *Ann.*, **501**, 49 (1933).
[135] W. H. Carothers and J. W. Hill, *J. Am. Chem. Soc.*, **54**, 1559 (1932).

acid, phenol, and other solvents. The observed small depressions in freezing point fluctuated capriciously as the solutions aged and frequently corresponded to molecular weights of one or a few glucosan units. All these data were interpreted as due to the partial or complete dissociation of associated complexes and to their spontaneous reversion to a more highly aggregated state.[127, 136, 137, 138] Although similar depressions were observed by others, the interpretation was not accepted because the values were found to fluctuate erratically instead of varying uniformly as the Hess theory demanded.[139, 140] Molecular weights were then determined by isothermal distillation through a porous plate[141, 142, 143] and in recent years it was found possible to eliminate the disturbing influence of the plate.[144, 145, 146] Today there is a tendency to concede that some of the effects observed by Hess and his collaborators are real and of great interest because they occur with numerous macromolecular materials. The isothermal distillation data appear, however, to have been of inadequate precision to have justified the conclusions drawn.[147] Staudinger and Schulz concluded that such depressions of freezing point and of vapor pressure were anomalous phenomena which gave no clue to the true weight of a macromolecular solute.[148] (See Chapter IX, B.)

If the association hypothesis was correct, one or other of the anhydro derivatives of 2,3,6-trimethylglucose should be capable of a reversible transformation to trimethylcellulose. Various methods of preparing these anhydrides led to conflicting results,[140, 149–152] but in the end it appeared that only one of the two possibilities IX and X had been synthesized and that

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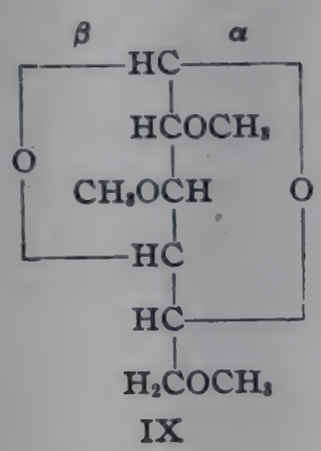
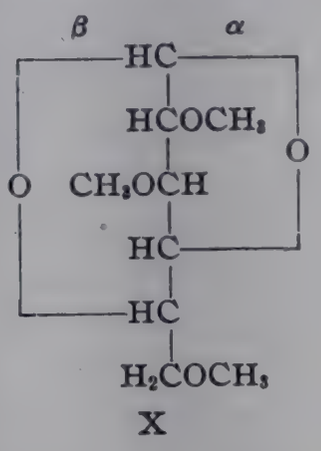
[136] K. Hess and G. Schultze, *Ann.*, **448**, 99 (1926).
[137] K. Hess and H. Friese, *Ann.*, **450**, 40 (1926).
[138] K. Hess and G. Schultze, *Ann.*, **455**, 81 (1927).
[139] M. Bergmann, E. Knehe, and E. Lippmann, *Ann.*, **458**, 93 (1927).
[140] K. Freudenberg and E. Braun, *Ann.*, **460**, 288 (1928).
[141] M. Ulmann, *Z. physik. Chem.*, **A156**, 419 (1931).
[142] M. Ulmann and K. Hess, *Ber.*, **66B**, 495 (1933).
[143] K. Hess and M. Ulmann, *Ann.*, **504**, 81; *Ber.*, **67B**, 2131 (1934).
[144] K. Hess and M. Ulmann, *Ber.*, **69B**, 1448 (1936).
[145] M. Ulmann, *Angew. Chem.*, **49**, 926 (1936).
[146] M. Ulmann, *Ber.*, **69B**, 1437 (1936).
[147] K. Hess and L. A. Surányi, *Z. physik. Chem.*, **A184**, 321 (1939).
[148] H. Staudinger and G. V. Schulz, *Ber.*, **70B**, 1577 (1937); see also numerous similar comments by other authors.
[149] F. Micheel and K. Hess, *Ber.*, **60B**, 1898 (1927).
[150] K. Hess and F. Micheel, *Ann.*, **466**, 100 (1928).
[151] K. Hess and O. Littmann, *Ber.*, **66B**, 774 (1933).
[152] K. Freudenberg and E. Braun, *Ber.*, **66B**, 780 (1933).

the very highly strained ring structure of the other made its existence unlikely. The 2,3,6-trimethyl-1,4-anhydroglucopyranose was a mobile, colorless oil, b. p., 83–85°/0.1 mm., that had the normal properties and showed no tendency to change into trimethylcellulose.[140] As an isomeric trimethylhexose anhydride with the required potentiality has not yet been isolated, this attempt to support the association theory was inconclusive.

Another obvious line of work was to change cellulose to the hypothetical glucosan required by Structure VIII ($x = 1$). Acetyl chloride in the presence of a trace of moisture dissolved cotton, and a chlorine-free cellulose acetate A was isolated in 90% yield.[127] Although this acetate gave apparent molecular weights of 2000 to 3000 in dilute phenol solution, its other prop-



IX



X

erties, together with those of its derivatives, show it to be merely slightly degraded cellulose acetate. The action of hydrogen bromide in acetyl bromide on the acetate of cellulose A, followed by deacetylation in moist chloroform-ether, was reported to give a nearly quantitative yield of a crystalline celloglucosan, $C_6H_{10}O_5 \cdot H_2O$.[127] An attempt to repeat this preparation, however, resulted not in celloglucosan but in a reputed anhydrotrihexosan which was first isolated as the crystalline nonaacetate and was considered to be the trimer of the expected compound.[153] Although this nonaacetate, on methylation and hydrolysis, gave a good yield of 2,3,6-trimethylglucose, its high specific dextrorotation of 86.6°, when contrasted with the small rotation of cellulose triacetate, rendered its relationship to the latter very questionable.

The dissolution of cotton in acetic anhydride and sulfuric acid was likewise considered to give a 90% yield of a crystalline biosan hexaacetate with an apparent molecular weight of 568 to 700 in sufficiently dilute acetic acid or phenol solution.[137, 154] It was later shown, from the specific vis-

[153] F. Micheel, *Ann.*, **456**, 69 (1927).
[154] K. Hess, *Ber.*, **54B**, 2867 (1921).

cosity,[155] the copper-reduction and acetyl values,[156] and the revised molecular weight,[157] that this biosan was really a mixture averaging about twelve glucose residues to the main valence molecule. Further work by Hess and his collaborators resolved the biosan fractions into crystalline limit dextrins I and II and a cellulose acetate II.[158] The trinitrate of the dextrin II gave with acetone a crystalline addition complex. X-ray data from the latter were considered to prove identity of the limit dextrin with native cellulose, the examination of which was complicated by its biological character and by the assumed presence of interpenetrating, morphological films of a noncellulose nature (*Fremdhautsystem*).[159, 160] The existence of these films has not been confirmed.

One of the corollaries of the "glucosan" theory was that copper-reducing derivatives like hydrocellulose or cellobiose were secondary products of little constitutional significance for cellulose. This inference was not accepted by the majority of those who adhered to the association theory. Very extensive work, particularly by Ost,[65] had set the maximum obtainable recovery of cellobiose octaacetate at 42–43%[161] and, since about one-third was degraded to glucose pentaacetate during the acetolysis, the original formation did not exceed 67% of the theoretical amount.[162, 163] Although this result was compatible with the random breakdown of a uniformly linked, linear macromolecule[162, 164] under the action of inorganic acid, it stood in stimulating contrast to the nearly quantitative yields of maltose obtainable from starch by a vital agent like the enzyme diastase. As a result of some studies with phosphorus pentabromide, Karrer suggested that both starch and cellulose were associated complexes based on a "cellosan" in which the glucosidic links united the 1,6- and the 1,4-positions of the two glucose residues. Although hydrolysis of the 1,6- linkage gave "cellobiose," the independent but concurrent scission of the 1,4- linkage would not do so and the yield of cellobiose would not be quantitative.[165] This

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[155] H. Staudinger and H. Freudenberger, *Ber.*, **66B**, 76 (1933).

[156] K. Freudenberg, *Ber.*, **62B**, 383 (1929).

[157] M. Bergmann and H. Machemer, *Ber.*, **63B**, 316 (1930).

[158] K. Dziengel, C. Trogus, and K. Hess, *Ann.*, **491**, 52 (1931).

[159] K. Hess, C. Trogus, and K. Dziengel, *Ann.*, **501**, 49 (1933).

[160] K. Hess, *Naturwissenschaften*, **22**, 469 (1934).

[161] H. Friese and K. Hess, *Ann.*, **456**, 38 (1927), claimed a 50–51% yield of cellobiose octaacetate.

[162] K. Freudenberg, *Ber.*, **54B**, 767 (1921).

[163] P. Karrer and F. R. Widmer, *Helv. Chim. Acta*, **4**, 174 (1921).

[164] J. Böeseken, J. C. Berg, and A. H. Kerstjens, *Rec. trav. chim.*, **35**, 320 (1916).

[165] P. Karrer and A. P. Smirnoff, *Helv. Chim. Acta*, **5**, 187 (1922).

suggestion was abandoned because the cellosan structure, on methylation and hydrolysis, would have given 2,3,6- and 2,3,4-trimethylglucose in equimolecular amount, instead of 100% of the former.[99] The name "cellosan" was afterwards adopted by Pringsheim and his collaborators for a reputed anhydroglucose triacetate prepared by heating cellulose triacetate in naphthalene at 235°C.[166] This work was shown to be erroneous.[167]

Bergmann and Knehe, in their acetolysis of cellulose with hydrogen chloride as a catalyst, isolated what they considered was the crystalline tetraacetate of a cellobiosan. Dilute solutions of this substance had the proper molecular depressions in some solvents and much lower ones, attributed to association, in others. The corresponding cellobiosan was insoluble in water but dissolved in alkali to give a yellow solution.[168] There is no doubt that this cellobiosan, like Hess and Friese's biosan, was a degraded cellulose mixture with an average molecular weight much greater than they thought.

In the course of their studies on the acetolysis of cellulose with sulfuric acid as a catalyst, Ost and his collaborators isolated a fraction which they regarded as a "celloisobiose or isocellobiose octaacetate" and which gave ordinary cellobiose octaacetate on rearrangement. On deacetylation, the "isocellobiose" crystallized with half a molecule of water and was a reducing carbohydrate with ordinary properties.[169, 170] Although Weltzien and Singer supported the individuality of Ost's "isocellobiose,"[171] it was presumed to be a mixture by Hess,[172] was not encountered by Zechmeister and Tóth,[173] and was shown to be a mixture of cellobiose and a new, reducing trisaccharide, "procellose," by Bertrand and Benoist.[174] "Procellose" proved to be identical with the substance now called cellotriose.[173] A second cellotriose prepared by Ost was probably an impure sample of the same substance,[175] the fully methylated derivative of which had previously been isolated in a nonhomogeneous condition by Irvine and Robertson.[176]

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[166] H. Pringsheim, J. Leibowitz, A. Schreiber, and E. Kasten, *Ann.*, **448**, 163 (1926).
[167] G. Schultze and K. Hess, *Ann.*, **450**, 65 (1926).
[168] M. Bergmann and E. Knehe, *Ann.*, **445**, 1 (1925).
[169] H. Ost and R. Prosiegel, *Z. angew. Chem.*, **33**, 100 (1920).
[170] H. Ost and G. Knoth, *Cellulosechem.*, **3**, 25 (1922).
[171] W. Weltzien and R. Singer, *Ann.*, **443**, 71 (1925).
[172] K. Hess, *Die Chemie der Zellulose*, p. 502; see ref. 1, p. 29.
[173] L. Zechmeister and G. Tóth, *Ber.*, **64B**, 854 (1931).
[174] G. Bertrand and S. Benoist, *Bull. soc. chim.*, [4], **33**, 1451 (1923); [4], **35**, 58 (1924). See also W. N. Haworth, E. L. Hirst, and O. Ant-Wuorinen, *J. Chem. Soc.*, **1932**, 2368.
[175] H. Ost, *Z. angew. Chem.*, **39**, 1117 (1926).
[176] J. C. Irvine and G. J. Robertson, *J. Chem. Soc.*, **1926**, 1488.

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The occurrence of a fully methylated anhydrotrisaccharide in Irvine and Robertson's mixture has not been confirmed.

Two other attempts to fit the experimental data to the association theory are worthy of record. Herzog and Jancke suggested that cellulose was an anhydrotetrasaccharide (Structure VIII, $x = 4$), largely because the x-ray diffraction pattern of the fibers contained four glucose residues in the unit cell.[177] Schorger, principally concerned with the yields of cellobiose and the presumed isocellobiose obtained in acetolysis, put forward a cyclic anhydrotetrasaccharide formula in which the linkages were of an acetal rather than the usual glucoside type.[178]

The failure of the adherents of Structure VIII to provide reproducible and decisive evidence in its support enhanced the attractiveness of the rival Formula VII, which had been favored throughout by many workers, including E. Berl, K. Freudenberg, W. N. Haworth, E. Heuser, R. Kuhn, H. Mark, K. H. Meyer, O. L. Sponsler, H. Staudinger, and R. Willstätter. General opinion was undecided in 1927,[179] but in the following years cellulose was degraded to a series of individual, crystalline fragments corresponding to $n = 3$ to $n = 5$ in Formula VII. The course of the degradation was proved to be in agreement with the random scission of equivalent bonds in a linear macromolecule.[180] It became possible to estimate the average molecular weights of such giant, main valence structures by improved measurements of osmotic pressure, by viscosity effects,[98] and by the ultracentrifuge.[181] The change in outlook became practically unanimous in 1932 when Haworth and Machemer isolated 0.6% of crystalline 2,3,4,6-tetramethylglucose from the hydrolysis products of a purified, carefully fractionated trimethylcellulose.[182] This scission product was the long-sought for[183] end group corresponding to VII and its amount indicated a chain containing at least 100 to 200 glucose residues. Organic chemists were thus brought into agreement with those who had claimed a somewhat similar chain length for cellulose on one interpretation of the x-ray data.[184, 185]

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[177] R. O. Herzog and W. Jancke, *Z. angew. Chem.*, **34**, 385 (1921).

[178] A. W. Schorger, *Ind. Eng. Chem.*, **16**, 1274 (1924).

[179] W. N. Haworth in *Chem. Soc. Ann. Reports*, **24**, 81 (1927); **25**, 106 (1928).

[180] K. Freudenberg, *Tannin, Cellulose, Lignin.* J. Springer, Berlin, 1933, p. 105.

[181] T. Svedberg and J. B. Nichols, *J. Am. Chem. Soc.*, **49**, 2920 (1927), discuss protein not cellulose.

[182] W. N. Haworth and H. Machemer, *J. Chem. Soc.*, **1932**, 2270.

[183] Earlier searches had given doubtful or negative results. See K. Hess and W. Weltzien, *Ann.*, **442**, 46 (1925) and refs. 99 and 100, p. 44, and ref. 140, p. 48.

[184] See H. Mark, *Trans. Faraday Soc.*, **29**, 42 (1933) and ref. 122, p. 46.

[185] H. Mark, *Physik und Chemie der Cellulose.* J. Springer, Berlin, 1932, p. 197.

The new physical methods, however, gave average molecular weights that were approximately tenfold greater, and there was a tendency to assume that the long-chain chemical entities "associated" or "aggregated" in solution to produce the still larger complexes found by physical measurements.[186] This assumption abruptly collapsed some years ago when it was discovered that Haworth and Machemer's trimethylcellulose had been degraded more extensively than had been thought possible during its preparation.[187, 188] Although repetition of the work yielded no tetramethylglucose from native cotton, the macromolecular structure was now so firmly established that the negative result was generally regarded, not as support for Structure VIII, but as proof that the main valence molecule of cellulose contained at least 700 glucose units. The last, basic divergence of opinion was thus resolved into the conclusion that cellulose was a linear macromolecule containing up to 3000 or 3500 units, that it dispersed to individual molecules in sufficiently dilute solutions, and that its physical properties were greatly influenced by a degradation too slight to be readily detected by the methods of organic chemistry.

It may seem at first sight surprising that the association theory retained its grip over the intellects of so many workers for so long a period. But it must be remembered that their intuition, although wrong in one dimension, was certainly right in two. Now that the thread-like nature of the cellulose molecule has been placed beyond question, future research will doubtless be mainly concerned with the association and the interplay of the secondary valence forces that radiate laterally from the cellulose chain.

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[186] This tendency was criticized by H. Staudinger and H. Freudenberger, *Ann.*, **501**, 162 (1933).

[187] K. Hess and F. Neumann, *Ber.*, **70B**, 728 (1937).

[188] W. N. Haworth, E. L. Hirst, L. N. Owen, S. Peat, and F. J. Averill, *J. Chem. Soc.*, **1939**, 1885.

B. CHAIN STRUCTURE

CLIFFORD B. PURVES

1. Quantitative Yield of Glucose from Cellulose

The first step in establishing the structure of cellulose was to demonstrate beyond doubt that the purest available form (cotton) yielded nothing but glucose when hydrolyzed. In order to carry conviction, it was necessary to recover the glucose, or a suitable derivative, in pure, crystalline condition and in nearly quantitative yield. Irvine and Soutar[1] attacked this problem by submitting cotton to acetolysis in the presence of a sulfuric acid catalyst. The highly degraded triacetates, together with an excess of methanol containing 0.5% of hydrogen chloride, were kept for 70 hours in sealed tubes at 100°C. This procedure simultaneously removed acetyl groups and completed the degradation of the cellulose to a crystalline mixture of methyl α- and β-glucopyranosides. The over-all recovery of the latter was 85% of theory and the identification was satisfactory. In the next attempt, Monier-Williams[2] used cold, 72% sulfuric acid to dissolve the cotton and completed the degradation to glucose by diluting the solution with much water and boiling under reflux for 15 hours. A 90.7% yield of crystalline glucose was obtained. Finally, Irvine and Hirst,[3] reverting to the acetylation technique, prepared cellulose triacetate in more than 99% yield from cotton by using small amounts of chlorine plus sulfur dioxide as a catalyst.[4] Methanolysis gave the crystalline, equilibrium mixture of the methyl α- and β-glucosides with the proper optical rotation and melting-point range. The mixture accounted for 95.5% of the cellulose after the weight of the latter was corrected for moisture and ash. The furfural test for pentosans was negative and compounds other than methyl glucoside

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[1] J. C. Irvine and C. W. Soutar, *J. Chem. Soc.*, **117**, 1489 (1920). This article pointed out technical weaknesses in the earlier claims.

[2] G. W. Monier-Williams, *J. Chem. Soc.*, **119**, 803 (1921); cf. H. Ost and L. Wilkening, *Chem.-Ztg.*, **34**, 461 (1910); H. Frahm, *Ber.*, **74B**, 622 (1941); H. H. Schlubach and E. Lührs, *Ann.*, **547**, 73 (1941).

[3] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **121**, 1585 (1922).

[4] W. L. Barnett, *J. Soc. Chem. Ind.*, **40**, 8T (1921).

were not detected. This work was generally accepted as decisive proof that pure cellulose consisted exclusively of glucose residues.

2. Nature of the Hydroxyl Groups in Cellulose

(a) *Number of Hydroxyl Groups*

The next lead in the structural study was contributed by Denham and Woodhouse[5, 6] who discovered that cotton, alternately soaked in 15% caustic soda and in dimethyl sulfate, slowly acquired methyl ether groups. Improved technique, including the use of 30% in place of 15% alkali, enabled Irvine and Hirst[7] to prepare a cellulose ether containing 42–43% of methoxyl groups in twelve treatments. The yield was reduced, mainly by manipulative losses, to 70% of theory. They noted that six additional methylations failed to increase the methoxyl content and concluded that the maximum possible degree of methylation corresponded to a trimethyl ether (OCH_3, 45.6%). Many later researches improved the methylation procedure until today it is possible to prepare almost completely methylated cellulose (OCH_3, about 45%) in 90% yield in a few operations.[8–11] Although the analyses for methoxyl in most of the earlier preparations tended to be slightly low owing to the method of estimation,[12] it still does not seem possible to bring the methoxyl content right up to the theoretical value of 45.6% without producing some degradation.[13, 14] Nothing eventuated, however, that threw doubt on the claim that the highest alkylated derivative was the trimethyl ether. This fact, in conjunction with the long-standing recognition that the highest acetate was a triacetate[15] and the highest nitrate a trinitrate,[16] showed beyond doubt that, on the average, cellulose contained three hydroxyl groups for each glucose residue.

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[5] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **103**, 1735 (1913). The principle of this method was made generally available for the alkylation of carbohydrates by W. N. Haworth, *J. Chem. Soc.*, **107**, 8 (1915).

[6] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **105**, 2357 (1914).

[7] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **123**, 518 (1923).

[8] K. Hess and W. Weltzien, *Ann.*, **442**, 46 (1925).

[9] E. Heuser and N. Hiemer, *Cellulosechem.*, **6**, 101, 125, 153 (1925).

[10] K. Freudenberg and E. Braun, *Ann.*, **460**, 288 (1928).

[11] W. N. Haworth, E. L. Hirst, and H. A. Thomas, *J. Chem. Soc.*, **1931**, 821.

[12] F. Neumann, *Ber.*, **70B**, 734 (1937); K. Freudenberg and H. Boppel, *Ber.*, **70B**, 1542 (1937).

[13] P. Karrer and E. Escher, *Helv. Chim. Acta*, **19**, 1192 (1936).

[14] G. G. Johnston, *J. Am. Chem. Soc.*, **63**, 1043 (1941).

[15] H. Ost, *Z. angew. Chem.*, **19**, 993 (1906).

[16] W. Crum, *Ann.*, **62**, 233 (1847); *Phil. Mag.*, **30**, 426 (1847).

Denham and Woodhouse[6] had hydrolyzed a methylated cellulose (OCH_3, 24–26%) in 43% hydrochloric acid and had obtained a new trimethylglucose in about 10% yield. This important result was soon checked by Irvine and Hirst,[7] who degraded their trimethylcellulose (OCH_3, 42–43%) in methanol containing 1% of hydrogen chloride at 100–130°C. for 100 hours. The resulting sirup, on distillation under diminished pressure, gave a methyl trimethylglucoside in 91.5% yield, corrected for the slightly low methoxyl content of the trimethylcellulose. Aqueous acid hydrolyzed the glucoside to the new crystalline trimethylglucose in a yield of 86%, which therefore corresponded to an over-all recovery of 78.7%. This result was considered to be a minimum value. Much experience with sugars showed that the introduction of the methyl ether group did not involve unforeseen alterations in molecular structure and that such groups remained in their original positions even under drastic conditions. It followed that in trimethylcellulose three methoxyl groups were attached to each glucose residue and that hydroxyl groups occupied the corresponding positions in cellulose itself. Moreover, since only one of the isomeric trimethylglucoses had been obtained, each glucose residue had its hydroxyl groups in the same three positions. Obviously, the next problem was to determine these positions.

(*b*) *Position of Hydroxyl Groups*

Denham and Woodhouse[6] noted that the new trimethylglucose failed to form a phenylosazone and correctly decided that the second position was occupied by a methoxyl group. Their conjecture that the sugar was substituted in the second, third, and sixth positions was subsequently confirmed by several arguments. Ruff and Ollendorff[17] had degraded the disaccharide lactose (4-(β-*D*-galactopyranosyl)-*D*-glucopyranose, Structure I, where **R** is the galactose residue) to a galactosyl-*D*-arabinose (II) that was still capable of forming a phenylosazone. The second position of the arabinose, corresponding to the third position of the original glucose unit, was therefore unsubstituted. When completely methylated lactose was hydrolyzed, one of the scission products was bound to be a trimethylglucose methylated in the second and third positions. Haworth and Leitch[18] showed that the trimethyl sugar derived from lactose was identical with that obtained from cellulose. Since the oxidation of the trimethylglucose with nitric acid gave a dimethylsaccharic acid (V) rather than a tri-

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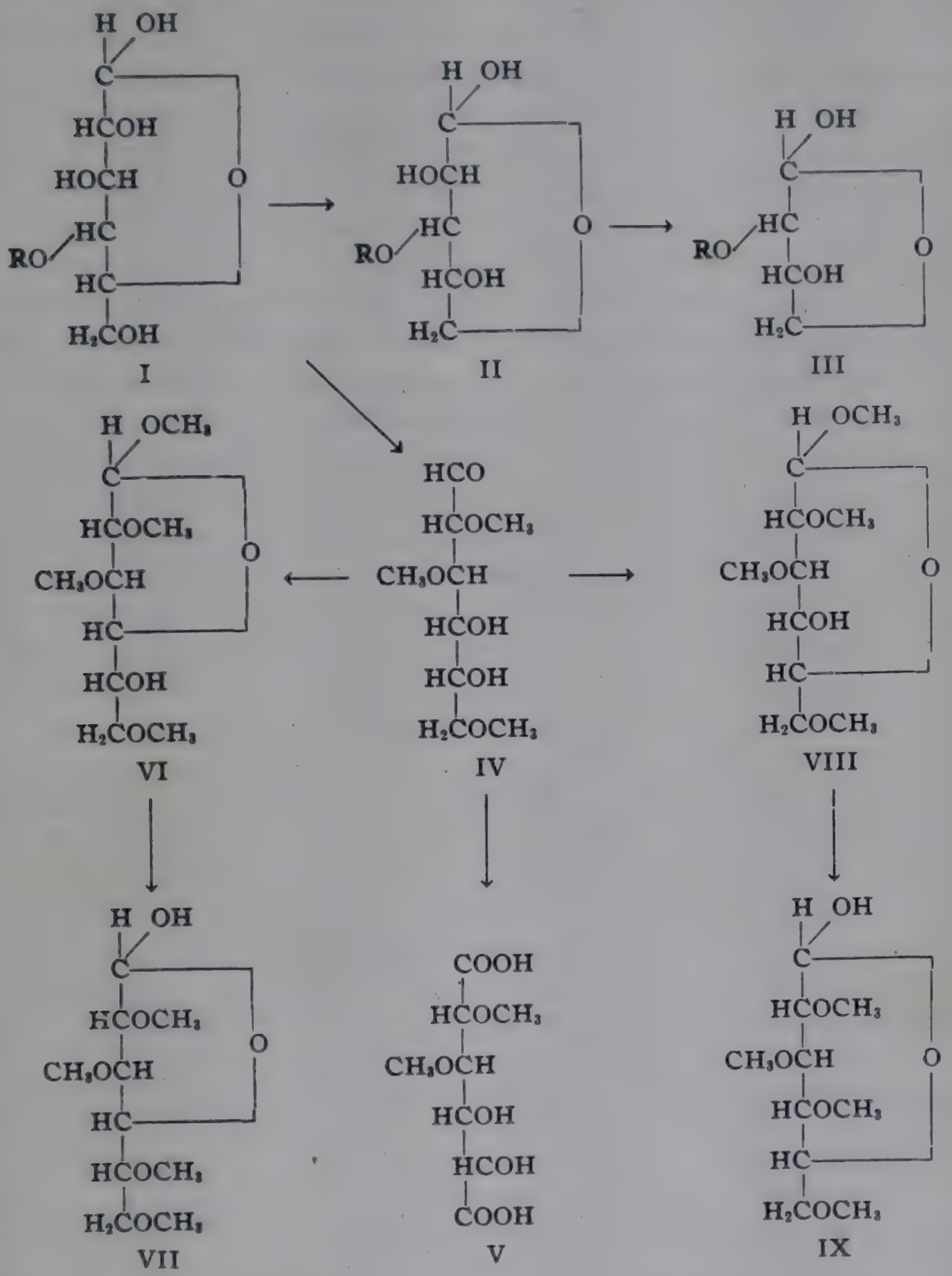
[17] O. Ruff and G. Ollendorff, *Ber.*, **33**, 1802 (1900).

[18] W. N. Haworth and G. C. Leitch, *J. Chem. Soc.*, **113**, 188 (1918).

methyl one, Irvine and Hirst[19] had no difficulty in deducing that the other methoxyl group had occupied the terminal or sixth position. In accord



with Irvine's system of nomenclature,[19] the trimethylglucose was indexed as the 2,3,6- isomer (IV). 2,3,6-Trimethylglucose occurred as fine needles.

[19] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **121**, 1213 (1922).

m. p. 122–123°C., and as short prisms, m. p. 92–93°C. The mutarotation in water was from $[\alpha]_D$ 90.2° to a final value of 70.5°, and from 117.7° to 88.6° in neutral methanol.[19]

More evidence in favor of this assignment was derived from the behavior of the sugar when dissolved in methanol containing 1% of hydrogen chloride. A complex change in optical rotation occurred at room temperature,[19] and when Schlubach and Bomhard[20] arrested the reaction near the minimum rotation, they isolated a levorotatory, sirupy mixture of methyl 2,3,6-trimethylglucosides (VI). Methylation, followed by hydrolysis of the glycosidic methoxyl group with mineral acid,[20, 21] gave the well-known, liquid tetramethylglucose (VII).[22] When the solution of the trimethylglucose in the acid methanol was boiled, a crystalline, somewhat less levorotatory methyl glucoside (VIII) was produced[23] which, on methylation and hydrolysis, yielded the still better known, crystalline tetramethylglucose (IX).[24, 25] These important results restricted the positions of the ring structures in the isomeric tetramethyl derivatives (VII) and (IX) to the 1,5- and 1,4- positions. When these ring structures were unambiguously determined by entirely independent methods worked out by Haworth, Hirst, and their collaborators,[26, 27] independent proof was forthcoming that 2,3,6-trimethylglucose could produce both 1,4- or furanose derivatives (VI) and 1,5- or pyranose ones (VIII). In other words, unmethylated hydroxyl groups were present in the fourth and fifth positions of the glucose skeleton.

Irvine and Rutherford[28] synthesized 2,3,6-trimethylglucose from methyl 2,3-dimethyl-α-glucopyranoside, the structure of which was known because the corresponding sugar formed no phenylosazone and gave L(+)-dimethoxysuccinic acid on oxidation with nitric acid. Nitration of the glycoside gave methyl 2,3-dimethyl-4,6-dinitro-α-glucoside (methyl 2,3-dimethyl-α-glucoside-4,6-dinitrate) and a subsequent iodination, with sodium iodide in acetone at 100°C., resulted in methyl 2,3-dimethyl-4-nitro-6-iodo-6-desoxy-α-glucoside (2,3-dimethyl-6-iodo-4-nitrate derivative). Replacement of the iodine atom by an acetate group, hydrolysis of the latter to hydroxyl, and methylation led to methyl 2,3,6-trimethyl-4-nitro-α-glucoside

[20] H. H. Schlubach and H. Bomhard, *Ber.*, **59B**, 845 (1926).
[21] J. C. Irvine and R. P. McGlynn, *J. Am. Chem. Soc.*, **54**, 356 (1932).
[22] J. C. Irvine, A. W. Fyfe, and T. P. Hogg, *J. Chem. Soc.*, **107**, 524 (1915).
[23] H. H. Schlubach and K. Moog, *Ber.*, **56B**, 1957 (1923).
[24] W. N. Haworth and E. L. Hirst, *J. Chem. Soc.*, **119**, 193 (1921).
[25] T. Purdie and J. C. Irvine, *J. Chem. Soc.*, **85**, 1049 (1904).
[26] W. Charlton, W. N. Haworth, and S. Peat, *J. Chem. Soc.*, **1926**, 89.
[27] E. L. Hirst, *J. Chem. Soc.*, **1926**, 350.
[28] J. C. Irvine and J. K. Rutherford, *J. Am. Chem. Soc.*, **54**, 1491 (1932).

(methyl 2,3,6-trimethyl-α-glucoside-4-nitrate). Iron dust in acetic acid reduced the nitrate to an hydroxyl group; acid hydrolysis removed the glycosidic methoxyl group, and crystalline 2,3,6-trimethylglucose remained.

3. Nature of the Linkages between the Glucose Units

The allocation of the hydroxyl groups in cellulose to the second, third, and sixth positions of the glucose residues left the mode in which the latter were linked together quite uncertain. The glucosidic bond might possess either the alpha or the beta configuration and might be attached to either the fourth or fifth position in the adjacent hexose unit. Denham and Woodhouse[29] were quick to realize that the latter alternative created doubt as to whether the hexose units possessed a 1,5- or 1,4- cyclic structure. In addition, the earlier x-ray data were erroneously held by Sponsler and Dore[30] to be consistent with a cellulose structure in which glucopyranose residues were united alternately by glucosidic 1,1- and by ether 4,4- oxygen linkages. The obvious way to clear up these uncertainties was to prepare and study scission products that were intermediate in complexity between cellulose and glucose. Cellobiose was the first of these products to be obtained in pure, crystalline form.

(*a*) *Cellobiose*

Hydrolysis of Cellulose to Cellobiose. The most advantageous method of preparing cellobiose octaacetate and, from it, the sugar itself,[31] is still based on the work of Franchimont,[32] who degraded cotton with acetic anhydride containing sulfuric acid. Skraup and König[33] demonstrated that Franchimont's crystals were the octaacetate of a new, reducing disaccharide consisting of two glucose residues and not fermented by yeast. The insensitivity toward yeast maltase, together with the ready hydrolysis to glucose brought about by emulsin,[34, 35] showed that the disaccharide linking in cellobiose had the beta configuration. The methylation of Skraup and König's crystalline methyl heptaacetyl-β-cellobioside,[33]

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[29] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **111**, 244 (1917).

[30] O. L. Sponsler and W. H. Dore, in *Fourth Colloid Symposium Monograph*. Chemical Catalog, New York, 1926, p. 174; *Chem. Abstracts*, **21**, 3268 (1927).

[31] G. Braun, *Organic Syntheses*. Vol. 17, John Wiley, New York, 1937, pp. 34, 36.

[32] A. P. N. Franchimont, *Rec. trav. chim.*, **18**, 472 (1899).

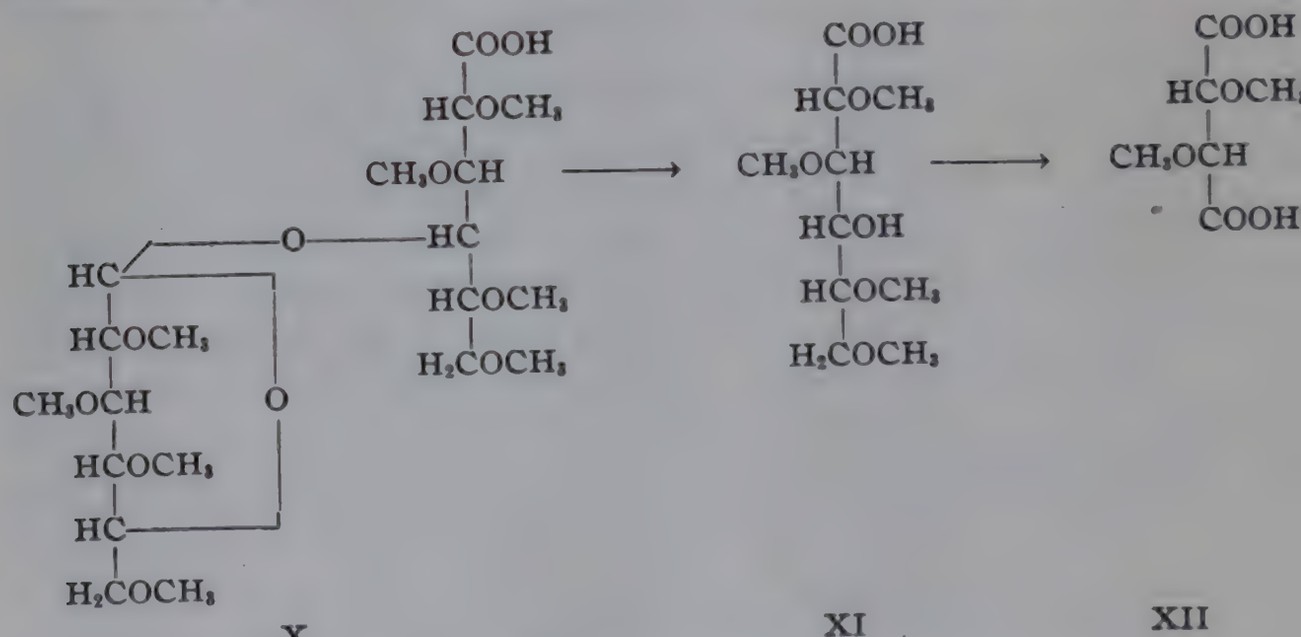
[33] Z. H. Skraup and J. König, *Monatsh.*, **22**, 1011 (1901).

[34] E. Fischer and G. Zemplén, *Ann.*, **365**, 1 (1909).

[35] N. K. Richtmyer and C. S. Hudson, *J. Am. Chem. Soc.*, **61**, 1834 (1939).

or of cellobiose itself,[24] gave the crystalline heptamethyl derivative[24, 36] which, upon acid hydrolysis, produced 2,3,4,6-tetramethylglucopyranose and 2,3,6-trimethylglucose in equimolecular amount.[24] This result restricted the structural possibilities for cellobiose to either 4- or 5-β-glucopyranosylglucose.

The first attempt to remove this ambiguity was due to Zemplén,[37] who prepared the oxime of cellobiose and degraded it by standard methods to the glucosylarabinose (Structure II, where **R** is the glucose residue). A repetition of the process led in poor yield to a sirupy glucosylerythrose (III) from which an osazone was *not* obtained. The second position in the erythrose, corresponding to the fourth in the original glucose unit, was accordingly considered to be blocked by the disaccharide linkage. This negative evidence was given positive confirmation by the work of Haworth, Hirst, and their collaborators.[38, 39] They eliminated the cyclic structure in the reducing half of cellobiose by oxidizing the disaccharide with bromine water to cellobionic acid. Complete methylation of the latter included the substitution of the position formerly occupied by the ring and resulted in octamethylcellobionic acid (X). Acid hydrolysis then gave a 92% yield of 2,3,4,6-tetramethylglucopyranose from the left-hand side of (X) and an 80% yield of a tetramethylgluconic acid from the right-hand side. This tetramethylgluconic acid was obviously either the 2,3,5,6- or the 2,3,4,6-



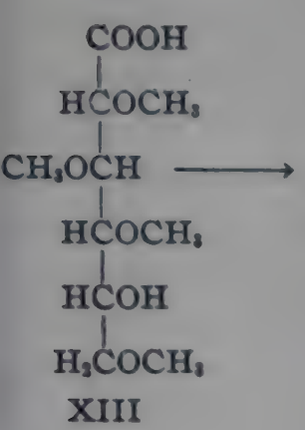
X XI XII

[36] P. Karrer and F. Widmer, *Helv. Chim. Acta*, **4**, 174 (1921). A crystalline methyl hexamethyl-β-cellobioside was also described.

[37] G. Zemplén, *Ber.*, **59B**, 1254 (1926).

[38] W. N. Haworth, C. W. Long, and J. H. G. Plant, *J. Chem. Soc.*, **1927**, 2809.

[39] W. N. Haworth, E. L. Hirst, and E. J. Miller, *J. Chem. Soc.*, **1927**, 2436.



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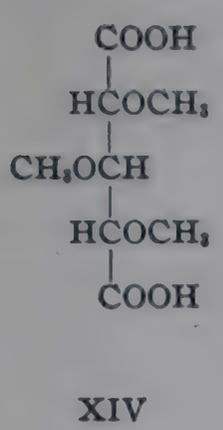

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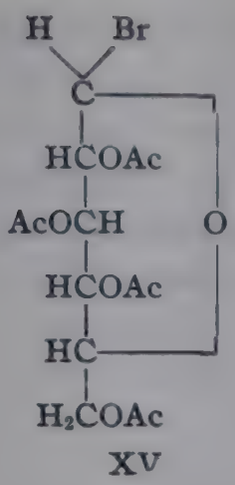

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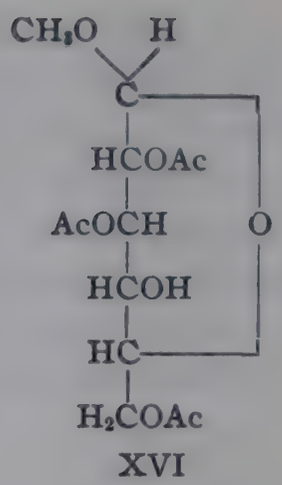

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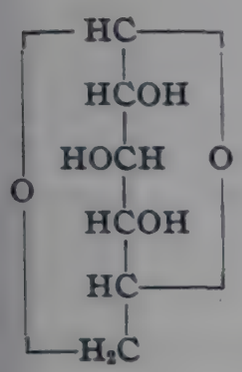

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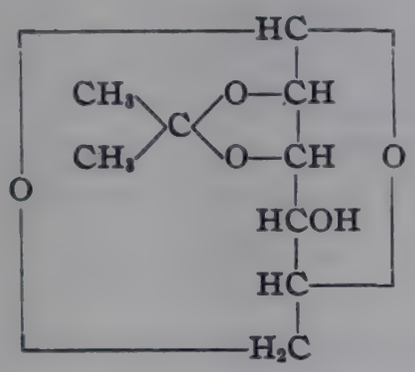

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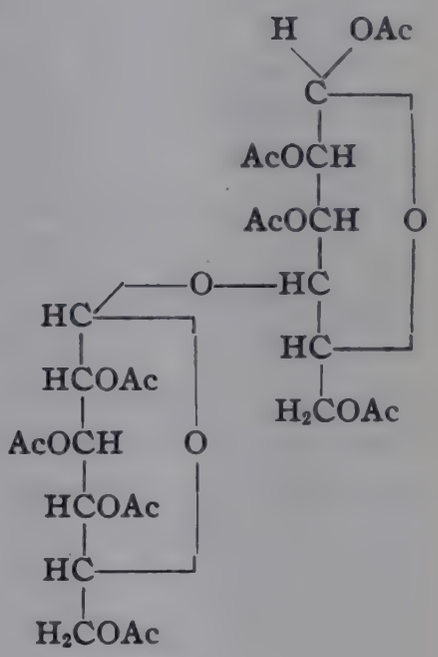

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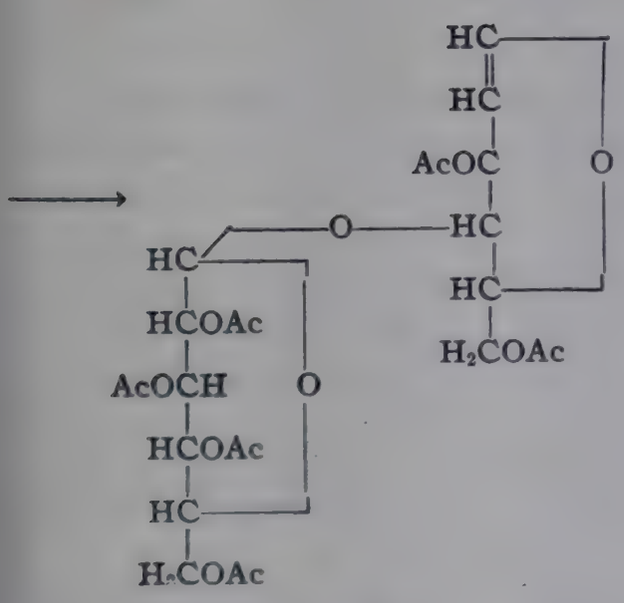

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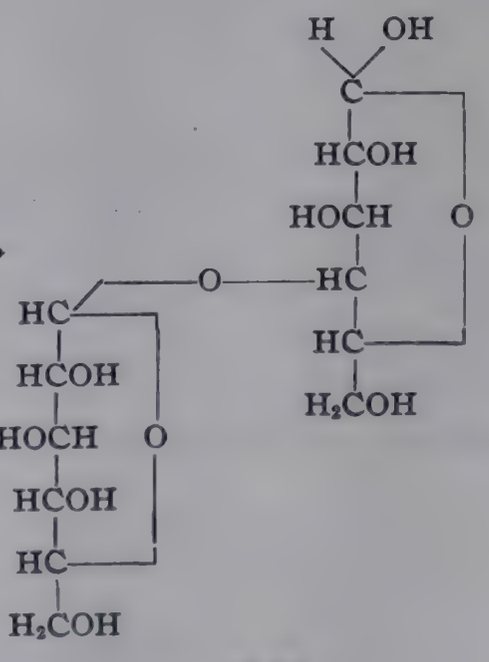

XXI

variety (XI or XIII) which had previously been obtained by the oxidation, with bromine water, of the sugars corresponding to the tetramethylglucosides (VI) and (VIII), respectively. On further oxidation with nitric acid, the 2,3,4,6- acid gave the trimethoxyglutaric acid (XIV) plus the dimethoxysuccinic acid (XII) in good yield. Only the latter could be expected, or was obtained, from (XI). When dissolved in water, 2,3,5,6-tetramethylgluconic acid (XI) came into equilibrium with its lactone at the comparatively slow rate characteristic of 1,4- lactones while the attainment of equilibrium between the 2,3,4,6- acid (XIII) and its 1,5-lactone was much more rapid.[26] 2,3,5,6-Tetramethylgluconolactone was a crystalline solid, m. p., 26–27°C., with a specific rotation of $[\alpha]_D$ 62.5° in water. The 2,3,4,6- lactone was an uncrystallized liquid with $[\alpha]_D$ 98°. The corresponding phenylhydrazides melted at 134–36°C. and 115°C., respectively. These facts determined the structure of the two tetramethylgluconic acids and made it clear that the one actually obtained from cellobiose was the 2,3,5,6- isomer (XI).[39] The disaccharide bond in cellobiose was therefore assigned to the fourth rather than to the fifth position, and the constitution of the disaccharide was definitely proved to be 4-(β-*D*-glucopyranosyl)-*D*-glucopyranose.

Syntheses of Cellobiose. Helferich and Bredereck[40] synthesized methyl heptaacetyl-β-cellobioside by condensing "acetobromoglucose" (2,3,4,6-tetraacetyl-β-*D*-glucosyl bromide) (XV) with methyl 2,3,6-triacetyl-β-glucopyranoside (XVI) in the presence of silver carbonate. The use, by Freudenberg and his collaborators,[41] of the corresponding methylated derivatives of glucose in the synthesis resulted in methyl heptamethyl-β-cellobioside. Freudenberg and Nagai,[42] however, were the first to synthesize cellobiose itself. They condensed "acetobromoglucose" (XV) with levoglucosan (1,6-anhydro-*D*-glucopyranose) (XVII) and obtained a mixture of partly acetylated anhydrodisaccharides in which the anhydro ring was known to be less stable toward acetolysis than the disaccharide linkage. Controlled acetolysis therefore produced some cellobiose octaacetate. Although the yields in these three syntheses were very small, the method used guaranteed that the disaccharide link in the products possessed the beta configuration and not the alpha. A much better synthetical route to cellobiose was discovered recently by Haskins, Hann, and Hudson[43]

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[40] B. Helferich and H. Bredereck, *Ber.*, **64B,** 2411 (1931).

[41] K. Freudenberg, C. C. Andersen, Y. Go, K. Friedrich, and N. W. Richtmyer, *Ber.* **63B,** 1961 (1930).

[42] K. Freudenberg and W. Nagai, *Ann.*, **494,** 63 (1932).

[43] W. T. Haskins, R. M. Hann, and C. S. Hudson, *J. Am. Chem. Soc.*, **63,** 1724 (1941)

when they condensed "acetobromoglucose" (XV) with the 2,3- monoacetone derivative of 1,6-anhydro-*D*-mannopyranose (XVIII). The crystalline product lost the acetone (isopropylidene) residue when heated with 80% acetic acid. Mild acetolysis opened up the 1,6-anhydro ring, and crystalline 4-(β-glucopyranosyl)-mannopyranose octaacetate (XIX) was obtained in an over-all yield of 20–25%. The remainder of the synthesis, leading from this acetate to the acetobromo derivative, to cellobial hexaacetate (XX), and to cellobiose (XXI),[44] had been investigated in the reverse direction by other workers.[45, 46]

(*b*) *Cellotriose, Cellotetrose, and Cellopentose*

Although the acetolysis of cotton was the favorite method of producing fractions intermediate in complexity between cellulose and cellobiose, it happened that the above series of homogeneous, sharply defined, crystalline substances was first obtained by an alternative method of degradation. Ordinary concentrated hydrochloric acid (38–39%) had occasionally been used to gelatinize and slowly dissolve cellulose,[47] but Willstätter and Zechmeister[48] noted that acid of about 41% concentration (d_4^{15} = 1.204 to 1.212) gave almost immediate solution at room temperature or lower. The results with hydrobromic (66%) and hydrofluoric acid (70–75%) were similar, but cotton did not dissolve in cold, concentrated hydriodic acid. When the freshly prepared, very viscous, nonreducing solution in hydrochloric acid was kept, the viscosity rapidly diminished, an ability to reduce an alkaline copper solution became apparent, and the optical rotation, at first practically zero, increased irregularly. The last two properties finally had values close to those observed in a control experiment with glucose.

In more extensive later work, Zechmeister and Tóth[49] dissolved 400 g. of purified cellulose in 4 kg. of the 42% acid at 15°C. Three to four hours thereafter, they interrupted the reaction by removing the acid as silver chloride and evaporated the liquor to 1800 cc. Alcohol, added in successive steps to give concentrations of 60, 85, and 90%, precipitated successive fractions weighing 53 g., 25 g., and 75 g., respectively. Similar opera-

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[44] W. T. Haskins, R. M. Hann, and C. S. Hudson, *J. Am. Chem. Soc.*, **64**, 1289 (1942).

[45] M. Bergmann and H. Schotte, *Ber.*, **54B**, 1564 (1921).

[46] W. N. Haworth, E. L. Hirst, H. R. L. Streight, H. A. Thomas, and J. I. Webb, *J. Chem. Soc.*, **1930**, 2636.

[47] E. Flechzig, *Z. physiol. Chem.*, **7**, 523 (1882–83).

[48] R. Willstätter and L. Zechmeister, *Ber.*, **46**, 2401 (1913).

[49] L. Zechmeister and G. Tóth, *Ber.*, **64B**, 854 (1931).

tions on the reconcentrated mother liquor precipitated a fourth fraction, 20 g., and the remainder was soluble in sufficient absolute alcohol. Each of these five fractions was refractionated from aqueous alcohol, fractions of similar optical rotatory and reducing power being combined, until at length homogeneous products were obtained. Cellobiose, 2 g., was isolated from the most-soluble fractions, which also contained glucose. Intermediate fractions gave 2 g. of a trisaccharide, cellotriose,[50] and 4.8 g. of a new tetrasaccharide, cellotetrose. Finally, the least-soluble fractions deposited nonhomogeneous cellodextrins and 2 g. of a new pentasaccharide, cellopentose. After recrystallization to constant rotation, the cellotriose and cellotetrose displayed the typical properties of mutarotating, copper-reducing, aldose sugars. Their molecular weights were determined from the freezing points of their aqueous solutions, by the titration of the aldose groups with hypoiodite, and by the analyses of their crystalline phenylosazones. Pyridine and acetic anhydride gave the crystalline, fully acetylated derivatives, and deacetylation restored the original sugars. The behavior of cellopentose was similar, except that the acetate crystallized in an unsatisfactory way, and the very soluble phenylosazone was not isolated. This sugar was at first mistaken for a hexasaccharide and was named cellohexose until Staudinger and Leupold[51] corrected the error. Others[52] doubted the homogeneity of the sugar. Zechmeister and Tóth[49] also submitted cellotriose to acetolysis and obtained cellobiose octaacetate. Cellotriose was therefore a cellobiosylglucose, and the entire series of oligosaccharides from cellobiose to cellopentose in all probability consisted of glucose residues uniformly linked together in an open chain for the cases $n = 2$ to $n = 5$ shown in Formula XXII. This type of plane projection was introduced by Haworth[53] and gives a much more accurate idea of the probable shape and stereochemical relationship of the glucose units in these polysaccharides than the more primitive formulas hitherto used (cf. VII or XXI).

In Formula XXII, if a β-glucopyranose residue is considered to have its carbon atoms one to five in the plane of the paper, the oxygen atom completing the ring is not in this plane. When viewed in perspective, the

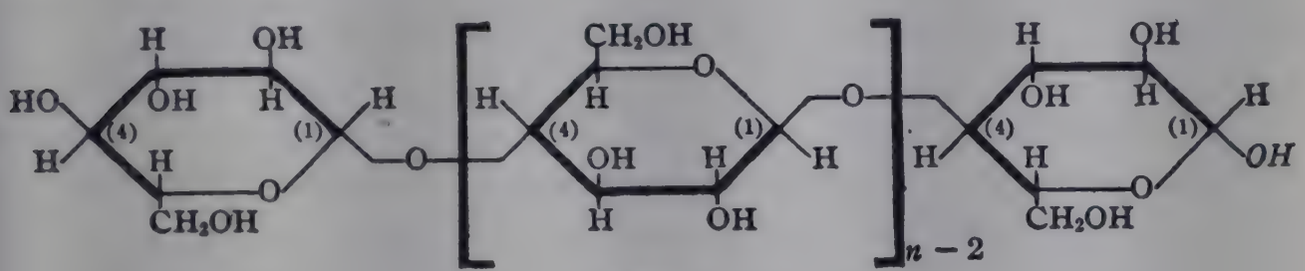
[50] Cellotriose and its acetate were first isolated, under the name of procellose, from an acetolysis of cellulose carried out by G. Bertrand and S. Benoist, *Bull. soc. chim.*, [4], **33**, 1451 (1923).

[51] H. Staudinger and E. O. Leupold, *Ber.*, **67B**, 479 (1934).

[52] K. Freudenberg, K. Friedrich, and J. Bumann, *Ann.*, **494**, 41 (1932).

[53] W. N. Haworth, *The Constitution of Sugars*. Edward Arnold, London, 1929, p. 90 and Plates I and II; see also G. V. Caesar and M. L. Cushing, *J. Phys. Chem.*, **45**, 776 (1941), especially Figs. 1–9.

hydroxyl groups and the glucosidic group are arranged above and below the plane of the paper in such a way that their distribution is completely trans. Molecular models, constructed with correct atomic volumes and atomic distances, strongly suggest that, when linked in the chain, the glucopyranose rings alternate in respect to the side that is uppermost. This inference, which is at once evident in Formula XXII from the alternating positions given to the primary alcoholic groups above and below the main chain, is supported by x-ray data. The models suggest that XXII can extend in a straight line and can also exist in large loops and coils, since the stereo arrangement permits of some rotation around the glucosidic bonds. There is no proof that the above ideas are necessarily correct in all details because strainless glucopyranose rings, if built on the Sachse-Mohr principle,[54] can theoretically exist in shapes other than the nearly planar one assumed here.



XXII

The structures of the substances corresponding to Formula XXII were checked by the methylation method for the cases $n = 3$ and $n = 4$. Haworth, Hirst, and Thomas[55] partly acetolyzed 20 g. of trimethylcellulose, dissolved the chloroform-soluble portion of the product in acetone, and replaced acetyl by methoxyl groups by means of dimethyl sulfate and alkali. Fractional distillation at 0.1-mm. pressure then separated the fully methylated methyl glycosides of glucose, cellobiose, and cellotriose from each other in yields of 15, 18, and 15%, respectively. Freudenberg, Friedrich, and Bumann,[52] who omitted the preliminary methylation of the cotton (100 g.) but otherwise followed a similar route, isolated the same substances in amounts of 7 g., 18 g., and 10 g., respectively. They were also successful in obtaining 5 g. of methyl hendecamethylcellotetroside. Finally, Hess and Dziengel[56] acetolyzed cotton, deacetylated the cellotriose fraction to the

[54] E. Mohr, *J. prakt. Chem.*, **98**, 315 (1918); **103**, 316 (1922).

[55] W. N. Haworth, E. L. Hirst, and H. A. Thomas, *J. Chem. Soc.*, **1931**, 824. Simultaneous deacetylation and methylation was also used by K. Freudenberg, *Ann.*, **433**, 230 (1923).

[56] K. Hess and K. Dziengel, *Ber.*, **68B**, 1594 (1935).

free sugar which they first purified (yield 9.9%), and then methylated completely. All three methods of preparation gave distilled fractions from which the same series of fully methylated methyl β-glycosides crystallized. Since Haworth, Hirst, and Thomas had started from trimethylcellulose, in which the substituents were very stable, the concordance of their results with those of the other two investigations eliminated all possibility of cellobiose or cellotriose, or their acetates, having been formed by some reversion process or obscure rearrangement during the degradation of the cellulose. Zechmeister and Tóth[49] had earlier come to the same conclusion because glucose behaved in no abnormal way when kept in the 43% hydrochloric acid they used to degrade cellulose.

The methyl β-glycosides of decamethylcellotrioside and hendecamethylcellotetroside had the correct molecular weights by Rast's method and contained the correct percentages of glycosidic, as opposed to ethereal, methoxyl groups.[52] The glycosidic group was derived from the copper-reducing, right-hand end of XXII and was evolved, as methanol, when the samples were heated with a mixture of acetic and hydrochloric acids.[57] The methanol that distilled was passed through the usual apparatus and was estimated as methoxyl. When the cellotrioside and the cellotetroside derivatives were hydrolyzed with aqueous acid, the final rotations of the solutions were close to those calculated for a mixture of 2,3,4,6-tetramethylglucopyranose (1 mole) and 2,3,6-trimethylglucose (2 or 3 moles). The first of these scission products corresponded to that expected from the left-hand end of XXII, while the moles of the second were correct for the $n - 1$ moles of trimethylglucose derived from the $n - 2$ middle units of XXII plus the right-hand one. These fragments were actually isolated from methyl decamethyl-β-cellotrioside in 96% and 84%, respectively, of the theoretical yields.[55] Another deduction from the Structure XXII was that the partial hydrolysis of the methylated cellotrioside should give heptamethylcellobiose and 2,3,6-trimethylglucose. This was the case.[55] In a repetition of the work by Klages,[58] the cellotrioside was heated for 90 min. at 98° in 0.4 *N* hydrochloric acid. The products isolated included some unhydrolyzed cellotrioside, some 2,3,6-trimethylglucose, 34% of the corresponding methyl β-glucoside, and 36% of methyl heptamethyl-β-cellobioside. Further proof of the constitution of methyl decamethyl-β-cellotrioside was provided by the synthetical work of Freudenberg and Nagai.[59] Benzyl

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[57] K. Freudenberg and K. Soff, *Ann.*, **494**, 68 (1932).

[58] F. Klages, *Ann.*, **520**, 71 (1935).

[59] K. Freudenberg and W. Nagai, *Ann.*, **494**, 63 (1932).

heptamethyl-β-cellobioside was hydrogenated over palladium to toluene and the reducing sugar, which was converted to a sirupy heptamethylcellobiosyl chloride. The latter, when condensed in the presence of silver carbonate with methyl 2,3,6-trimethyl-β-glucopyranoside, gave the fully methylated derivative of methyl β-cellotrioside. Although the yield was modest, this synthesis showed that cellotriose was a β- rather than an α-glycoside of cellobiose and that the linkage occupied the fourth position in the reducing unit of the trisaccharide. Tables 1, 2, and 3 contain summaries of the principal physical constants observed in the cellobiose-cellopentose series. Other physical data which have been obtained include

TABLE 1

DATA ON THE CELLOBIOSE-CELLOPENTOSE SUGARS AND ON CELLULOSE

	Cellobiose	Cellotriose	Cellotetrose	Cellopentose	Cellulose
Max. yield, %[a]	40[31]	9.9[56]	1.2[49]	0.5[49]	.....
Crystal form [49]	Needles[60]	Microneedles	Same	Same	Micelles
M. p., °C.[49]	225[60]	238[b]	251	266	>270
Soly. in water, %[49]	.....	25[56]	12.5	5	Insol.
$[\alpha]_{589}^{18}$ in water[c, 49]	(+16°)–(+35.0°)[61]	(+31.8°)–(+23.2°)	(+11.3°)–(+17°)	(+11.4°)–(+12.6°)	.....
$[\alpha]_{578}^{18}$ in 51% H_2SO_4[68]	+43.3°	+32°	+25°	+13.5°	+2°
Hydrolysis const.[d]					
10^4 K at 18°	1.07	0.636–0.64	0.506–0.52	.....	0.305
at 30°	6.94	4.5–4.6	3.65–3.8	.....	2.34
10^3 *U*	27.3	28.6	28.9	.....	29.8
10^{16} *A*	3.4	18	24	.....	67
Acetolysis const.[62]					
10^4 K	1.7	.....	.....	.....	3.9 ± 0.3
Phenylosazone[49]					
M. p., °C. (decomposes)	198°	208° (uncor.)	228°	.....	.....
$[\alpha]_D^{20}$ in abs. C_2H_5OH	−20°	−16.3°	−41°	.....	.....

[a] Actually isolated in pure form.

[b] Hess and Dziengel[56] give m. p. 202–203°C. These melting points depend on the mode of heating, and decomposition occurs.

[c] The first value was observed up to 15 min. after contact of water with the sugar and the second value was after the mutarotation was complete.

[d] Freudenberg and Blomqvist[68] determined these first-order constants K for the initial stage of hydrolysis in 51% aqueous sulfuric acid by extrapolation. The activation energies *U* and the steric factors *A* were calculated from the K values at 18° and 30°C. and the relationship $K = Ae^{-U/RT}$.

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[60] F. C. Peterson and C. C. Spencer, *J. Am. Chem. Soc.*, **49**, 2822 (1927).

[61] C. S. Hudson and E. Yanovsky, *J. Am. Chem. Soc.*, **39**, 1013 (1917).

[62] K. Freudenberg and K. Soff, *Ber.*, **66B**, 19 (1933).

x-ray studies of some or all of the sugars themselves, their acetates,[63, 66] and their fully methylated methyl β-glycosides.[67]

TABLE 2

PHYSICAL PROPERTIES OF THE CELLOBIOSE-CELLOPENTOSE ACETATES AND OF CELLULOSE ACETATE

(Ref. 49, except as noted)

Acetates of:	Cellobiose	Cellotriose	Cellotetrose	Cellopentose	Cellulose
Crystal form	Small needles	Needles[63]	Microneedles	Doubtful	Micelles
M. p., °C., α-form	229.5°	219–220°[66]	α,β-Mixture	.....	>280°
β-form	202°	209–210° (cor.)	225° (cor.)	.....	Decomposes
$[\alpha]_{589}$ in $CHCl_3$					
α-form	+42.0°[65]	+22.4°[a, 66]	α,β-Mixture	α,β-Mixture	−22°[64]
β-form	−14.5°[65]	−18.2°[66]	−15.6°	−7.6°	0.0144
Viscosity,[51] η_{sp}[b]	0.0233	0.0182	0.0164	0.0144	

[a] Rotational data are given for several other solvents.
[b] The specific viscosity is calculated per glucose residue in 1.4% meta-cresol solution at 20°C.

TABLE 3

PHYSICAL PROPERTIES OF THE METHYLATED METHYL β-GLYCOSIDES OF THE CELLOBIOSE-CELLULOSE SERIES

(Ref. 52, except as noted)

	Cellobiose	Cellotriose	Cellotetrose	Cellulose
Yield, %, from cellulose	18[55]	<15[55]	<3.5	.....
Crystal form	Needles	Big needles	Microneedles	X-ray micelles
B. p., °C., 0.1 mm.	160–165°	215–225°	260–270°	>300° (decomp.)
M. p., °C.	87–88°	118°	139°	~215–216°[11]
$[\alpha]_{578}$ in $CHCl_3$	−15.2°	−11.3°	− 9.8°	−4.5° (?)
in H_2O	−16.5°	−17.0°	−16.1°	−19.1°
in CH_3OH	−16.2°	−15.5°	−15.5°	−14°
in 50% H_2SO_4[a]	− 7.5°	− 2.4°	0.3°	9.7°

[a] Extrapolation to initial rotation.

4. Uniformity of the Glycosidic Bonds in Cellulose

(a) *Chemical Proof of Structure*

The systematic application of the powerful analytical tool called the methylation method revealed the structures of the methylated derivatives

[63] G. J. Leuck and H. Mark, *J. Am. Chem. Soc.*, **56**, 1959 (1934).
[64] K. Hess and G. Schultze, *Ann.*, **455**, 81 (1927).
[65] C. S. Hudson and J. M. Johnson, *J. Am. Chem. Soc.*, **37**, 1276 (1915).
[66] L. Zechmeister and G. Tóth, *Ber.*, **68B**, 2134 (1935), discussed other x-ray data.
[67] T. Ohasi, *Bull. Chem. Soc. Japan*, **14**, 517 (1939); *Chem. Abstracts*, **34**, 2229 (1940).

f glucose, cellobiose, cellotriose, cellotetrose, and cellulose. The first hree were synthesized by methods that checked their constitution and what vas known of cellopentose strongly suggested that it, too, fitted into the ellobiose-cellulose series. This concordant and extensive mass of research was regarded by Freudenberg as amounting to a *chemical proof* of he constitution of cellulose.[68, 69]

(*b*) *Polarimetric Proof of Structure*

As Zechmeister and Tóth[49] pointed out, the physical data in Tables 1, 2, nd 3, when read from left to right, suggest that Formula XXII denoted ellulose when n was assumed to be very large. It is true that the recorded otations of the phenylosazones (Table 1) do not alter in a regular way but his anomaly may be due to the fact that osazones mutarotate. The riginal qualitative form of Zechmeister and Tóth's suggestion, however, y no means ruled out the possibility of variations in the chain, such as the ccurrence of a few glycosidic bonds in the alpha, rather than the beta, conguration or linked to the fifth, rather than to the fourth, position in the eighboring glucose unit. Freudenberg and his collaborators[52, 68] argued hat if the chain were entirely uniform, its molecular rotation would be an dditive function of the rotations contributed by its individual constituent nits. Since the molecular weight of cellulose was unknown, it was necesary to calculate the molecular rotations for each glucose unit before pplying this deduction from the principle of optical superposition. Multiplication of the specific rotations in Tables 1, 2, and 3 by the appropriate nolecular weights gave the molecular rotations, $[M]_n$, from which the nolecular rotation for each glucose residue was readily obtained by dividng by the total number (n) of glucose residues in the molecule. If the eft-hand end of Structure XXII had the rotation $[M]_e$, the right-hand aldehyde end $[M]_a$, and any intermediate unit $[M]_i$, then the molecular rotaion of any member of the series with n units was:

$$[M]_n = [M]_e + (n - 2)[M]_i + [M]_a$$

nd the rotation for each glucose unit was:

$$\frac{[M]_n}{n} = \frac{[M]_e + [M]_a}{n} + \frac{n - 2}{n} \cdot [M]_i$$

When the chain became infinitely long and n in consequence infinitely large,

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[68] K. Freudenberg and C. Blomqvist, *Ber.*, **68B**, 2070 (1935). This article summarizes he chemical, polarimetric, kinetic, and static proofs for the constitution of cellulose.

[69] K. Freudenberg, *Tannin, Cellulose, Lignin.* J. Springer, Berlin, 1933, pp. 97–106.

the latter expression reduced to $\frac{[M]_\infty}{\infty} = [M]_i$. In other words, the molecular rotation contributed by any intermediate residue in the chain was equal to that of an infinitely long chain, calculated for each glucose unit. This deduction merely amounted to the statement that the rotational contribution of the two ends of a very long chain could be neglected. The above equation therefore became:

$$\frac{[M]_n}{n} = \frac{[M]_e + [M]_a}{n} + \frac{n-2}{n} \cdot \frac{[M]_\infty}{\infty}$$

Since the experimentally observed value for cellobiose corresponds to: $\frac{[M]_e + [M]_a}{2}$, the following equation may be written:

$$\frac{[M]_n}{n} = \frac{2}{n}\left(\frac{[M]_2}{2}\right) + \frac{n-2}{n}\left(\frac{[M]_\infty}{\infty}\right)$$

Assuming that the observed value for cellulose was $\frac{[M]_\infty}{\infty}$, it was possible to calculate the molecular rotations of compounds of intermediate chain lengths such as cellotriose ($n = 3$) or cellotetrose ($n = 4$). Conversely, the rotations of the latter made it possible to compute that of cellulose. Table 4 shows the results of such calculations.

After division by the molecular weight of a glucose unit, the calculated molecular rotations become the specific rotations of cellulose or its derivative. The value of about $-2°$ for cellulose in water is very plausible, although the insolubility of the polysaccharide made it impossible to check this deduction directly. The concordance between the calculated values was surprisingly good in view of the fact that the rotations of the equilibrium mixtures of the reducing sugars were used in the calculations. Perhaps the most reliable figures were obtained with the fully methylated methyl β-glycosides, which were pure, crystalline, chemical individuals. These data agreed with each other and with the observed values to within 1°, except for one chloroform and one water value, which diverged by 2° and 4°, respectively. Since the specific rotations of trimethylcellulose and trimethylstarch differ by about 250°,[52] because starch is an α-glycosidic analog of cellulose, the alteration of one bond in every hundred from the β- to the α-glycoside configuration in the trimethylcellulose chain would increase the rotation by about 2.5°. A systematic discrepancy of this magnitude between the observed and calculated data was not present but would have been easy to detect. Taken as a whole, the agreements

TABLE 4

MOLECULAR ROTATIONS PER GLUCOSE UNIT IN THE CELLOBIOSE-CELLULOSE SERIES

Solvent	Cellobiose		Cellotriose		Cellotetrose			Cellopentose				Cellulose						
	$\frac{M}{2}$	$\frac{[M]_2}{2}$	$\frac{M}{3}$	$\frac{[M]_3}{3}$	$\frac{M}{4}$	$\frac{[M]_4}{4}$ (found)	$\frac{[M]_4}{4}$ (calculated)	$\frac{M}{5}$	$\frac{[M]_5}{5}$ (found)	$\frac{[M]_5}{5}$ (calculated)		$\frac{M}{n}$	$\frac{[M]_n}{n}$ (found)	$\frac{[M]_n}{n}$ (calculated)			$[\alpha]$ (found)	$[\alpha]$ (calculated) (average)
Rotations of the Unsubstituted Sugars										*d*	*e*			*d*	*e*	*f*		
Water[a, b]	171	+5990°	168	+3900°	166.5	+2830°	+2855°	165	+2150°	+2230°	+2200°	162	...	−280°	−330°	−410°	...	−2.1 ± 0.4°
51% H_2SO_4[c]	171	+7400°	168	+5400°	166.5	+4200°	+4400°	165	+2230°	+3800°	+3560°	162	+320°	+1400°	+1000°	−1220°	+2.0°	+7.4 ± 1.2°
Rotations of the Acetates in Chloroform																		
α-Acetate[a]	339	+14,240°	322	+7210°	314	...	+3700°	308	...	+1590°	...	288	−6340°	−6840°	...	...	−22.0°	−22.2°
α,β- Mixtures[a]	...	...	322	+2320°	314	−4900°	...	308	−2340°	...	...	288	...	...	...	...	...	...
β-Acetate[a]	339	−4910°	322	−5860°	314	...	−6330°	308	...	−6620°	...	288	...	−7760°	...	...	...	−25.2°
Rotations of the Methylated Methyl β-Glycosides																		
Chloroform	227	−3450°	219	−2480°	216	−2120°	−2000°	208	...	−1600°	−1850°	204	−920°	−540°	−790°	...	−4.5°	−3.3 ± 0.7°
Water	227	−3740°	219	−3720°	216	−3470°	−3710°	208	...	−3700°	−3420°	204	−3900°	−3680°	−3200°	...	−19.1°	−17.1 ± 1.2°
Methanol	227	−3680°	219	−3390°	216	−3350°	−3250°	208	...	−3160°	−3280°	204	...	−2810°	−3020°	...	...	−14.2 ± 0.6°
50% H_2SO_4	227	−1700°	219	−530°	216	+70°	+50°	208	...	+410°	+420°	204	+1990°	+1810°	+1840°	...	+9.8°	+9.0°

M = molecular weight; $[\alpha]$ = specific rotation; $[M] = M[\alpha]$ = molecular rotation; n = number of glucose units in chain.

[a] Wave length of light used for measuring rotation was 589 mμ. In other cases λ = 578 mμ.

[b] Equilibrium rotations.

[c] Initial rotations.

[d] From cellobiose and cellotriose, by equation: $$\frac{[M]_n}{n} = \frac{2}{n}\left(\frac{[M]_2}{2}\right) + \frac{n-2}{n}\left(\frac{[M]_\infty}{\infty}\right)$$

[e] From cellobiose and cellotetrose, as in Note *d*.

[f] From cellobiose and cellopentose, as in Note *d*.

were so close that Freudenberg concluded that the cellulose chain must possess the uniformity assumed in the calculation. The work accordingly amounted to a *polarimetric proof* of the constitution of cellulose.

(*c*) *Kinetic Proof of Structure*

If the glycosidic bonds in cellulose were equivalent, it should also be possible to account quantitatively for the course of the changes in optical rotation and in reducing power produced by acid hydrolysis. Freudenberg, Kuhn, and their collaborators set themselves this task.[68] Glucose, cellobiose, cellotriose, and cellotetrose were separately dissolved in aqueous $51 \pm 0.2\%$ sulfuric acid, and all the solutions were 0.05 molar (9 g. per liter) in glucose when hydrolysis was complete. Duplicate solutions were kept at 18 and 30°C., and the gradual increase in the number of reducing groups was followed by means of titrations with alkaline hypoiodite solution. Optical rotations were simultaneously observed in a 2-dm. tube, and 10,000 times the observed rotation equalled the molecular rotation for each glucose unit in each case. For convenience, Freudenberg replaced the factor 10,000 by the factor 100, corresponding to an unusual definition of molecular rotation in which one gram mole was dissolved in 100 cc. of solution. The hypoiodite titration and the rotation of the glucose solutions remained practically unchanged throughout the experiment.

The titrations determined the fraction, α, of the glycosidic bonds that had undergone hydrolysis at any time, t, and the application of the first-order rate equation, $K = \frac{1}{t} \log \frac{1}{(1 - \alpha)}$, gave the average value of the rate K during the first t minutes of the hydrolysis. Extrapolation to zero time then gave the initial rates K_2, K_3, K_4, reported in Table 1 for cellobiose, cellotriose, and cellotetrose. In the case of cellobiose, the rate remained unchanged throughout the hydrolysis. With cellotriose, a systematic variation became apparent as hydrolysis proceeded. Reference to Formula XXII ($n = 3$) makes it clear that the left-hand glycosidic bond in cellotriose belongs to an unsubstituted glucopyranose unit, whereas the right-hand bond originates in a unit substituted in the fourth position. Since these two bonds very probably hydrolyzed at somewhat different rates, Freudenberg and Kuhn assumed that whichever one happened to break first in a given cellotriose molecule did so at a rate equal to the average initial observed rate, K_3. Use was then made of the fact that the cleavage of either bond produced cellobiose, which then underwent scission at the uniform rate K_2. The mathematical implications of these

deas were worked out by Kuhn[70] as:

$$1 - \alpha = \frac{K_2 - K_3}{K_2 - 2K_3} e^{-2K_3 t} - \frac{K_3}{K_2 - 2K_3} e^{-K_2 t}$$

This formula[71] gave calculated values of $1 - \alpha$ that agreed excellently with those observed by the hypoiodite method throughout the entire course of the hydrolysis. The degree of hydrolysis, α, at any time, t, was also predicted correctly from the optical observations by the use of an analogous formula involving the molecular rotations of glucose, cellobiose, and cellotriose.[68]

The hydrolysis of cellotetrose (XXII, $n = 4$) was more complicated, because here three different types of bonds were present. The two end bonds might be justifiably expected to cleave at an average rate of K_3 and, in either case, the subsequent scission of the cellotriose unit so formed would continue along the lines already described. If the middle bond of the tetrasaccharide broke first, two molecules of cellobiose, hydrolyzing at the rate K_2, would be formed. The course of the degradation of cellotetrose obviously depended on the ratio, q, of K_3 to the rate, K_m, at which the middle bond hydrolyzed. Kuhn[70] showed that the degree of hydrolysis, α, was given by an elaborate exponential function involving q, K_2, K_3, K_4, and the time t. All these quantities were known except q and trial showed that the calculated $1 - \alpha$ versus time plot was not very sensitive to the exact value of this ratio. The calculated titration and polarimetric plots were in very satisfactory agreement with the experimental ones at 18°C., either when K_4 was taken as 0.52×10^{-4} (Table 1) and q was 1.4 or when K_4 was 0.506×10^{-4} and q was 0.8. The agreement was also satisfactory for the hydrolyses at 30°C. and the most probable value for q, both at 18 and 30°C., was considered to be 1.4 to 1.6.

Surgical cotton, 0.05 glucose units as in the other cases, was quickly dissolved in 65% sulfuric acid and the solution was diluted to one liter of 51% acid as soon as it was possible to do so without precipitating dextrins.[68] The hydrolysis was followed optically and by hypoiodite titrations and the initial rate constant, K_n, was obtained by extrapolation from the titration data as already described. Mathematical limitations forced the use of

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[70] W. Kuhn, *Ber.*, **63B,** 1503 (1930), Formula 11 b. Other assumptions on the course of the degradation are also treated mathematically. The formulas are reproduced by H. Mark, *Physik und Chemie der Cellulose*. J. Springer, Berlin, 1932, pp. 293–5.

[71] W. Kuhn, C. Molster, and K. Freudenberg, *Ber.*, **65B,** 1179 (1932), pointed out that if the left- and right-hand bonds in triglycine (or cellotriose) hydrolyze at rates K_α and K_β, the average observed rate K_3 is $(K_\alpha + K_\beta)/2$. K_1 is written for K_3 in the original article.[70]

simplifying assumptions when attempts were made to calculate the form of the rate plots. The most successful of these hypotheses was that when the long chain disintegrated, all glycosidic bonds adjacent to the reducing ends of the various-sized fragments broke at the rate K_2, and all other bonds in the fragments hydrolyzed at the rate K_n initially observed for cellulose itself. An approximate mathematical expression for $1 - \alpha$ was worked out by Klages[72] and an exact one by Kuhn[73, 74] which expressed $1 - \alpha$ as an exponential function involving K_2, K_n, and t. When the calculated plots of $1 - \alpha$ against time were compared with those obtained experimentally at 18 and 30°C., both by the hypoiodite and the optical rotation methods, the agreement was within the experimental error for almost the whole course of the hydrolyses. The authors were careful to point out, however, that the mathematical assumptions underlying the work were only an approximation to the truth. For example, the calculated values of K_3 and K_4 at 18°C. were $(K_2 + K_n)/2$ and $(K_2 + 2K_n)/3$ or 0.69×10^{-4} and 0.56×10^{-4}, respectively, whereas the observed values were 0.64×10^{-4} and 0.52×10^{-4} (Table 1). An assumption still closer to reality would be that the glycosidic bonds at *both* ends of each disintegrating chain fragment were hydrolyzed at an average rate equal to K_3 and that K_n applied to all the middle links. The initial rate of hydrolysis of cellotetrose would then be $(2K_3 + K_n)/3$ or be 0.515×10^{-4} at 18°C., in excellent agreement with the observed value of 0.506 to 0.520×10^{-4} (Table 1). All these rate constants were of the magnitude characteristic of glucopyranosides and the same remark was true of the corresponding activation energies. The drift in the latter from cellobiose to cellulose (Table 1), however, was possibly due to experimental error because Moelwyn-Hughes[75] reported the activation energy for the hydrolysis of cellobiose between 60 and 80°C. as 30,970, instead of Freudenberg's value of 27,300 calories.

Freudenberg and his collaborators regarded the above rate studies as a *kinetic proof* of the constitution of cellulose because the assumption was that all the hydrolyzable links in a long-chain molecule were equal and equivalent except the one at each end. This assumption was the same as that underlying the polarimetric proof. Although the results fell within the rather narrow limits of the experimental errors, the truth may be that

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[72] F. Klages, *Ber.*, **65B**, 302 (1932); *Z. physik. Chem.*, **A159**, 357 (1932).

[73] K. Freudenberg and W. Kuhn, *Ber.*, **65B**, 484 (1932). K_1 is written for K_n.

[74] W. Kuhn, *Z. physik. Chem.*, **A159**, 368 (1932). K_1 is written for K_n.

[75] E. A. Moelwyn-Hughes, *Trans. Faraday Soc.*, **25**, 503 (1929); see K. Freudenberg, *Trans. Faraday Soc.*, **32**, 74 (1936).

the intermediate bonds differ very slightly according to their proximity to the end of the chain, tending to resemble those in an "infinite" chain (cellulose) when toward the middle, and grading toward those in cellobiose or cellotriose when very close to an end.[68] The validity of these arguments was increased by the fact that $1 - \alpha$ versus time plots for the hydrolysis of cellulose could be calculated from other assumptions with results that diverged from the observed ones.[68, 70] These other possibilities included the assumption that cellulose contained two types of glycosidic bonds that hydrolyzed independently at different rates; or that cellulose consisted of nonreducing, anhydrodisaccharide units that associated by means of secondary valence forces to aggregates of colloidal size.

(*d*) *Static Proof of Structure*

The polarimetric and kinetic proofs depended greatly upon extrapolation from the structures and the physical properties of cellobiose, cellotriose, cellotetrose, and cellopentose, but the degradation of cellulose gave inconsiderable yields of all these sugars except cellobiose. This serious objection to the proofs was satisfactorily overcome by considerations originating with Freudenberg[76] and later put into a mathematical form by Kuhn.[70, 77] If all the glycosidic bonds in the very long cellulose chain, including those at both ends of all degraded segments, hydrolyzed at the same rate, scission would occur quite at random along the chain, and fragments of all possible intermediate lengths would soon result. As all fragments more complex than glucose were subject to further hydrolysis, the amount of one of given length, say cellotetrose, would pass through a maximum as hydrolysis proceeded. Kuhn found that for a definite degree of hydrolysis, α, the yield of the j-membered fragment was $j\alpha^2(1 - \alpha)^{j-1}$ and that the maximum yield occurred when α was $2/(j + 1)$. These relationships showed that the random breakdown of a long, uniform chain could not possibly produce more than 18.7, 13.8, and 11.0% of cellotriose, cellotetrose, and cellopentose, respectively. This fact completely explained the low yields of these derivatives reported in Table 1. Cellobiose octaacetate, however, was isolated by acetolysis in 42–43% of theory whereas the above calculation put the maximum possible amount at 29.8%. The difficulty was quickly traced to the fact that the ready crystallization of the substance from the acetolysis solution protected much of it from further

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[76] K. Freudenberg, *Ber.*, **54B**, 767 (1921).

[77] H. Mark, *High Polymers*, Vol. 2, *Physical Chemistry of High Polymeric Systems*. Interscience, New York, 1941, p. 327.

degradation, and that in consequence the above relationships did not apply. Further calculation showed that, if cellobiose octaacetate were completely stable in the reaction mixture, no more than 66.7% would be formed. This figure made the maximum isolated yield of 42–43% entirely reasonable and completed what came to be called the *static proof* of the constitution of cellulose. The proof was not quite rigorous in the form described above because all glycosidic bonds in the chain fractions were assumed to be equivalent and the bonds at either end were known to hydrolyze rather more rapidly than the others. When allowance was made in the calculations for this factor, the maximum yields were altered by trivial percentages and the validity of the static proof was in no way impaired. In the acetolysis experiments, for example, the rate constants given in Table 2 suggested that the maximum yield of cellobiose octaacetate was 70 ± 1% instead of the 66.7% calculated by neglecting the end groups. The acetolysis rate constants were obtained as already described for aqueous hydrolysis but the final rotations of the solutions diverged substantially from each other and also from that attained by the glucose control.[62] These discrepancies were traced to the fact that acetolysis produced not only the expected mixture of 2,3,4,6-tetraacetyl-α- and -β-*D*-glucopyranose acetate but also varying amounts of open-chain, heptaacetylgluconic aldehyde.[78]

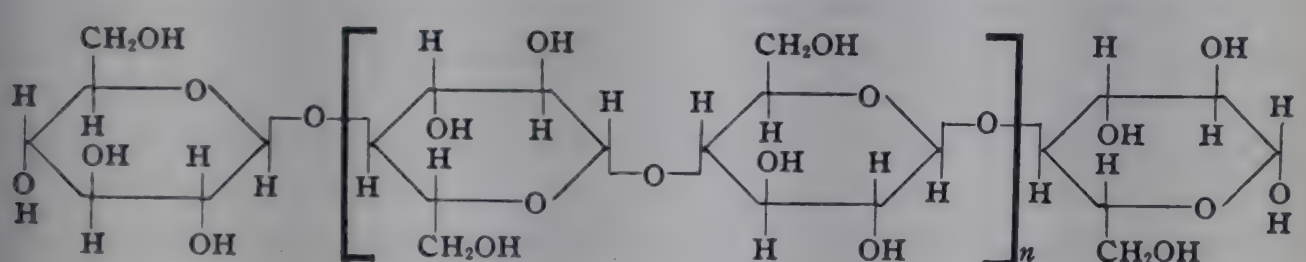
To sum up, the cumulative effect of the chemical, polarimetric, kinetic, and static proofs was to answer every reasonable objection to the assignment of the linear Structure XXII to the original unaltered cellulose as it occurs in the plant. The agreement between experimental and calculated values in the polarimetric and the kinetic proofs was so close that at least 99% of the glycosidic bonds were equivalent and of the 4-β-glucoside type exemplified by those in cellobiose or cellotriose. The proofs assumed that the chain length of cellulose was infinite. This assumption was obviously nothing more than a mathematical convenience and it was necessary to establish the true length of the chain by other methods. It is also necessary to emphasize that the structural proofs failed to determine the nature and location of perhaps 1% of the glycosidic linkages. Any variation or relative chemical weakness in such linkages might occasion variations of much greater consequence in the physical properties of cellulose.

[78] K. Freudenberg and K. Soff, *Ber.*, **70B**, 264 (1937).

C. END GROUPS

ARNOLD M. SOOKNE AND MILTON HARRIS

According to the present-day generally accepted concept, evidence for which has been summarized in the preceding section, cellulose consists of long chains of the condensation products of β-glucose as shown in the following scheme:



It is apparent from this structure that both terminal glucose residues are distinguished from those in the body of the chain, one by the presence of a reducing hemiacetal group, the other by the presence of an extra hydroxyl group. The presence of the former type of group in native cellulose has never been conclusively demonstrated but possible reasons for this will be presented later. The presence of the extra hydroxyl group at the nonreducing end appears to have been proved.

Cellulose, as it is generally encountered in industry, is in a more or less degraded form and for this reason, depending on the type of degradation, may or may not have end groups such as those described above. If the degradation is produced by strictly hydrolytic cleavage of the cellulose chains, then the system will remain unchanged from the standpoint of types of end groups. Thus, at each point of cleavage, one reducing and one nonreducing type of terminal group are formed. On the other hand, cleavage of the chains by other degradation processes, such as by oxidation (see Section I, 3 of this chapter) may result in the formation of very different types of terminal groups, which up to the present time have not been completely elucidated.

From the foregoing, it is seen that the determination of the number and type of terminal groups is of interest not only from the point of view of the

molecular structure and average chain length of the molecules, but also from the technological point of view. In addition, since a number of the methods for end-group determination involve measurement on undissolved cellulosic materials, the data gained from them regarding molecular chain length are also of interest in that they provide confirmation of results obtained by physicochemical methods which involve assumptions relative to the state of solution of the material.

The various methods which have been used in investigations of the end groups are discussed in the following sections.

1. Reducing Type of End Group

A number of methods have been proposed for the estimation of this type of group but it must be emphasized that interpretation of the results obtained with these methods in terms of molecular chain lengths involves the following assumptions: (1) each chain contains a terminal hemiacetal group; (2) all of the reducing power is contributed by these terminal groups; (3) the method used produces no new terminal groups through cleavage processes. In general, all of these assumptions are open to question as will be brought out in the subsequent discussion.

The most widely used method has been the well-known "copper number" method of Schwalbe.[1] The method depends on the reduction of copper from the cupric to the cuprous state by the cellulosic material. The original procedure has been frequently modified, but, despite numerous improvements, it still leaves much to be desired. Thus, the copper number obtained for a particular sample has been shown to depend on such factors as temperature of heating,[2] time of heating,[3] ratio of weight of sample to weight of solution,[2, 4] physical state of the sample (fineness of cutting or grinding),[5, 6] composition of the solution containing the cupric ion,[3] solubility of the Cu_2O formed in the mother liquor,[2, 7] and the progressive degradation of the cellulose by the alkaline solutions employed.[8] For these

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[1] C. G. Schwalbe, *Ber.*, **40**, 1347 (1907).
[2] C. J. Staud and H. LeB. Gray, *Ind. Eng. Chem.*, **17**, 741 (1925).
[3] A. Koechler and M. Marqueyrol, *Ann. chim. anal. chim. appl.*, **10**, 349 (1928).
[4] D. A. Clibbens and A. Geake, *Shirley Inst. Mem.*, **2**, 383 (1923).
[5] H. Staudinger and E. Archer, *Ber.*, **69B**, 1090 (1936).
[6] K. Atsuki and I. Kagawa, *Cellulose Ind.* (Tokyo), **9**, 11, 88 (1933).
[7] W. A. Richardson, R. S. Higgenbotham, and F. D. Farrow, *J. Textile Inst.*, **27**, T131 (1936).
[8] L. Brissaud, *Mém. poudres*, **25**, 244 (1932–3).

reasons, the copper number at best can be considered to be only a rough measure of the content of reducing groups of a cellulosic material. The results obtained by this method, however, have more significance when the method is applied to a homologous series of samples prepared by similar treatments.

A similar method which depends on the reduction of silver from the ionic to the metallic state by the cellulosic material was brought forth by Götze.[9] There are not sufficient data available for a complete evaluation of the method, but it is apparent that the amount of silver reduced increases indefinitely with the time of treatment, and no satisfactory method of correcting for this effect is available.

Another group of methods depends on the reaction of the reducing aldehyde groups with reagents that form condensation products with these groups. In the method of Staud and Gray,[10] the cellulosic material is allowed to react with phenylhydrazine acetate, and the nitrogen content of the product is taken as a measure of the number of reducing groups. It was shown by these authors that an equilibrium value of the nitrogen content can be reached, and that there is fair agreement between phenylhydrazine numbers and copper numbers for a series of widely different samples. The method has the advantage that the cellulose is probably not severely degraded during the treatment. However, since the samples used by these investigators were not characterized by other measurements, it is difficult to evaluate the quantitative aspects of the method. The increase in nitrogen content of a cellulosic material after reaction with phenylhydrazine was also used by Bergmann and Machemer[11] as a measure of content of reducing end groups. They obtained good agreement between the content of reducing groups as determined by this method, and by their iodometric method which is discussed below. In addition, there have been numerous efforts to measure the content of reducing groups of hydro- and oxy-celluloses by reacting the material with substituted hydrazines, sodium bisulfite, and other reagents that form condensation products with aldehyde groups. Reference to these methods is made elsewhere (see Section I, 3 of this chapter).

The reaction of cellulose with ethyl mercaptan in the presence of fuming hydrochloric acid was used by Wolfrom and coworkers to determine the number of free aldehydic end groups produced in the progressive degrada-

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[9] K. Götze, *Melliand Textilber.*, **8**, 624, 696 (1927).

[10] Z. C. Staud and H. LeB. Gray, *Ind. Eng. Chem., Anal. Ed.*, **1**, 80 (1929).

[11] M. Bergmann and H. Machemer, *Ber.*, **63B**, 316 (1930).

tion of cotton.[12, 13, 14, 15] Under the conditions of their experiments, the reaction

$$RCHO + 2EtSH \rightarrow RCH(SEt)_2 + H_2O$$

takes place, and the extent of mercaptal formation is indicated by the sulfur content of the cellulosic product. The molecular weights of the mercaptalated products as a function of the time of reaction were determined by both sulfur and viscosity determinations, and the correspondence between these values indicates that the method is a reliable measure of end groups. Because of the continual degradation of the sample by the strong acid solution used, it is necessary to extrapolate to zero time to obtain an estimate of the degree of polymerization of the starting material. An extrapolated value of 400 was obtained for the average degree of polymerization of a methylcellulose obtained by methylation of a commercial cellulose acetate, but no estimate for the molecular weight of native cellulose has been obtained by this method.

The most promising methods, from a quantitative standpoint, depend on the ability of alkaline iodine solutions to oxidize the reducing aldehyde groups to carboxyl groups. Such methods involve relatively simple volumetric procedures, in sharp contrast with the laborious procedures for estimating the nonreducing terminal groups. They suffer, however, from the disadvantages common to most heterogeneous reactions.[16] The first application of this reaction to cellulosic materials was made by Bergmann and Machemer[11, 17] after they had demonstrated that it gave stoichiometric results with aldohexoses, disaccharides, and a number of sugar acetates. The claims of these investigators that the iodine consumed by cellulose is selectively confined to the oxidation of free aldehyde groups to carboxyl groups, and that the reaction is of a stoichiometric nature have been disputed, especially by Hess and his coworkers,[18] Brissaud,[19] and Sakurada.[20] The principal criticisms have been that the consumption of

[12] M. L. Wolfrom and L. W. Georges, *J. Am. Chem. Soc.*, **59**, 282 (1937).

[13] M. L. Wolfrom, L. W. Georges, and J. C. Sowden, *J. Am. Chem. Soc.*, **60**, 1026 (1938).

[14] M. L. Wolfrom and J. C. Sowden, *J. Am. Chem. Soc.*, **60**, 3009 (1938).

[15] M. L. Wolfrom, J. C. Sowden, and E. N. Lassettre, *J. Am. Chem. Soc.*, **61**, 1072 (1939).

[16] A. R. Martin, L. Smith, R. L. Whistler, and M. Harris, *J. Research Natl. Bur. Standards*, **27**, 449 (1941); *Am. Dyestuff Reptr.*, **30**, 628 (1941).

[17] M. Bergmann and H. Machemer, *Ber.*, **63B**, 2304 (1930).

[18] K. Hess, K. Dziengel, and H. Maass, *Ber.*, **63B**, 1922 (1930).

[19] L. Brissaud, *Mém. poudres*, **25**, 222 (1932–3); **27**, 214 (1937).

[20] I. Sakurada, *J. Soc. Chem. Ind. Japan*, **36**, suppl. binding, 279 (1933).

iodine does not cease at any given time but proceeds more or less indefinitely, and, accordingly, that the reaction is not stoichiometric.

More recently, the method has been reinvestigated by Martin, Smith, Whistler, and Harris[16] who found that the above-mentioned criticisms were valid. A study of the factors which influenced the consumption of iodine by glucose and by cotton celluloses revealed that the values obtained depended on a number of conditions: for example, the length of time the reaction was allowed to proceed, the temperature, and the *p*H values of the iodine solutions. On the basis of these experiments, studies on the rate of oxidation of hydrocellulose at 0°C. and *p*H 10.6 were undertaken. It was found that there is an initial rapid reaction in the first hour followed by a secondary reaction during which iodine is consumed at a very much lower but practically constant rate. Purified cotton cellulose showed only a slight initial reaction with iodine, but after 1 hr. exhibited a secondary reaction of the same rate as the hydrocellulose. By applying a correction for the amount of iodine consumed in the secondary reaction, it was possible to estimate the iodine utilized in the oxidation of aldehydic groups. Iodine utilized in this way converted aldehydic to carboxylic groups, and, accordingly, an independent check of the value obtained with iodine was readily obtained by the estimation of the carboxyl groups thus formed (methods for estimating carboxyl groups are described in Sections G and H of this chapter).

Application of this method to cotton, purified with a 1% solution of sodium hydroxide for 8 hrs. according to the procedure of Corey and Gray,[21] indicated that purified cotton does not contain a measurable number of terminal reducing groups. However, the possibility that aldehyde groups may have been present in the cellulose before purification of the fiber cannot be overlooked, although some arguments against this possibility have been presented.[22]

Since hydrolytic degradation of cellulose results in the formation of a reducing group at each point of cleavage, the method also offers a means of estimating molecular weights at various stages of degradation by use of the following equation:

$$\mathbf{M}_n = \frac{W}{n\left(1 + \frac{\alpha \mathbf{M}_{n_0}}{162}\right)} \quad .$$

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[21] A. B. Corey and H. LeB. Gray, *Ind. Eng. Chem.*, **16**, 853 (1924).

[22] A. M. Sookne and M. Harris, *J. Research Natl. Bur. Standards*, **26**, 205 (1941); *Am. Dyestuff Reptr.*, **30**, 107 (1941).

where

$\mathbf{M}_n$ = the number-average molecular weight
$\mathbf{M}_{n_0}$ = the number-average molecular weight of the original sample
W = the weight of cellulose
n = the number of moles of cellulose originally present
α = the degree of hydrolysis = fraction of the original glucosidic linkages which have been hydrolyzed

Application of the method[16] to a series of progressively degraded hydrocelluloses, the value of n being determined viscometrically, yielded molecular-weight values which were in good agreement with those determined from viscosity measurements. The agreement between the molecular weights must to some extent be regarded as fortuitous since the viscosity method gives weight-average molecular weights, while the end-group method gives number-average values. Nevertheless, the proportionality between the molecular weights as obtained by the two methods is significant, and indicates that the iodometric method furnishes a good measure of relative molecular size.

2. Nonreducing End Groups

As pointed out earlier, one terminal group of the cellulose chain shown in the figure on p. 77 is characterized by four alcoholic hydroxyl groups. This is also true of celluloses degraded by hydrolytic means but probably not for celluloses degraded by oxidative reagents.

The presence of the extra hydroxyl group in the terminal glucose residue has been the basis for many attempts to estimate molecular chain length since, on complete methylation of cellulose, such a terminal group would yield tetramethylglucose. Denham and Woodhouse[23] early reported a trace of crystalline material in the hydrolysis product of a methylated cellulose which resembled tetramethylglucose, but later work on methylated celluloses did not confirm their observations. Irvine and Hirst,[24] and Freudenberg and Braun[25] were also unable to find any trace of tetramethylglucose. This led the former investigators to postulate a ring structure for cellulose and the latter to the conclusion that the molecular chains of cellulose are very long. Haworth and Machemer[26] were the first definitely to isolate tetramethylglucose as the methyl glucoside derivative through a

[23] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **105**, 2357 (1914).
[24] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **123**, 518 (1923).
[25] K. Freudenberg and E. Braun, *Ann.*, **460**, 288 (1928).
[26] W. N. Haworth and H. Machemer, *J. Chem. Soc.*, **1932**, 2270.

process which involved acetylation of the cellulose, conversion of the acetate to a completely methylated product, hydrolysis of the methylated cellulose, and finally conversion of the methylated glucose components into the methyl glucosides which were separated by fractional distillation. It was claimed that this procedure produced little or no scission of the chain molecules, and, on the basis of the results, it was concluded that cellulose was composed of chains of an average length of 100 to 200 glucose residues, the average of these values being regarded as the average lower limit of the size of the molecules.

The interpretation of the results of this type of experiment in terms of the molecular weight of the starting material involves the following assumptions:

(1) Each chain contains a terminal glucose residue capable of yielding tetramethylglucose. This is probably true for undegraded celluloses and hydrocelluloses, but for certain oxycelluloses the modification of the terminal glucose residue may be such as to render it incapable of the formation of tetramethylglucose.

(2) The tetramethylglucose is contributed solely by the terminal glucose residues described in (1). This assumption is justifiable.

(3) The procedure used produces no new terminal groups through cleavage of the molecular chains. This is probably never completely true, although it would appear that degradation may be kept low by proper control of conditions. Since for undegraded cellulosic materials the proportion of terminal groups appears to be of the order of magnitude of one part in several thousand, it is apparent that even a relatively minor amount of degradation may lead to erroneous results. The possibility of degradation must therefore be considered very carefully.

The method of Haworth and Machemer[26] has been criticized by Hess and Neumann[27] on the grounds that the starting material (acetone-soluble cellulose acetate) is unsuitable for a determination of the end groups in cellulose, since a certain amount of degradation must occur in the acetylation and saponification processes. Furthermore, Hess and Neumann were unable to remove the cleavage products so obtained or to separate quantitatively the tetramethylglucose from the trimethylglucose by Haworth and Machemer's method of fractional distillation of the respective glucosides. It is difficult to evaluate these criticisms, especially since repetition of the method of Haworth and Machemer by other members of Haworth's school led to complete substantiation of the original results.[28] It seems

[27] K. Hess and F. Neumann, *Ber.*, **70B**, 710 (1937).

[28] F. J. Averill and S. Peat, *J. Chem. Soc.*, **1938**, 1244.

reasonable, however, to agree with Hess and Neumann's criticism concerning degradation during acetylation and saponification, especially in view of the very low average degree of polymerization (D.P.) for cellulose obtained by the use of this method in comparison with values obtained by other methods.

On the basis of their criticisms of the method of Haworth and Machemer, Neumann and Hess[29] developed a method which differs from the method of Haworth and Machemer in that the methylation is performed directly on the cellulose, and, in the separation of the glucosides, recourse is had to the fact that the barium salts of the phosphoric esters of the methyl trimethylglucoside and less highly methylated sugars are insoluble in petroleum ether, while that of the methyl tetramethylglucoside is completely soluble. The Neumann and Hess methylation procedure yields a product of 42% methoxyl content, corresponding to complete methylation of only about 72% of the glucose units; this must therefore be taken into account in calculations of the number of end groups in the original material.

The procedure has been applied by Hess and Neumann to various relatively undegraded samples of cotton. It was found that when air was carefully excluded during the alkaline purification pretreatment as well as during the subsequent methylation, no tetramethylglucose was obtained. It was therefore concluded that natural cotton cellulose contains no end groups, and consists of chains of infinite length, or, more probably, of ring structures. A similar result was later obtained on ramie.[30] The presence of air during the alkaline pretreatment or during the methylation was found to produce numerous end groups.

The results of Hess and Neumann were substantiated by Leckzyck,[31] who reported, in addition, that thorough extraction (in the absence of air) with 9% NaOH is necessary to remove completely the fat-wax concomitants of the natural fiber, which may otherwise appear in the end-group fraction. Further, Leckzyck prepared an artificial mixture of methyl tetramethyl- and methyl trimethyl-glucosides in the proportion of 1 : 9300 and found that the loss of the former was only 7.7%. It was accordingly claimed that the method is at least sensitive enough to determine end groups if they appear in the proportion of only 1 part in 10,000. It is well to note, however, that Hess's data show an appreciable loss of the methyl tetramethylglucoside during the distillation processes when artificial mixtures

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[29] F. Neumann and K. Hess, *Ber.*, **70B**, 721 (1937).
[30] K. Hess and K. P. Jung, *Ber.*, **73B**, 980 (1940).
[31] E. Leckzyck, *Ber.*, **71B**, 829 (1938).

are used.[29, 32] When the number of steps in the purification process is considered, as well as the variety and quantity of complex cleavage products which may be present, the likelihood of such losses appears to be great. It is perhaps indicative of the inherent difficulties of the isolation methods that Averill and Peat[28] have substantiated Haworth and Machemer, but have been unable to repeat the results of Hess and Neumann. The most recent claims of Hess's school[33] place the minimum D.P. of cellulose at 10,000; the weight-average D.P. of cotton as obtained by Kraemer from viscosity measurements is approximately 3500.

In subsequent studies, Haworth and coworkers improved their method of fractional distillation for the separation of the methyl glucosides.[34] They also met the criticisms of Hess by directly methylating the cellulose, and by working in an atmosphere of nitrogen.[35] Their new data show that when relatively undegraded cotton is methylated in an atmosphere of nitrogen, no tetramethylglucose is found in the hydrolysis products.[35] Somewhat paradoxically, however, they reported an end-group content corresponding to an average D.P. of 700 for a sample of cotton sliver which had been directly methylated in an atmosphere of nitrogen for fifteen successive times.[36] It must be noted, however, that the series of methylation treatments produced a large decrease in the viscometrically determined chain length. Their present (minimum) value for the average D.P. of natural cellulose (700), while considerably higher than their earlier estimates, still leaves a very large discrepancy between their results and those of Hess's school.

Experiments by Haworth and collaborators on hydrocellulose[37] and oxycellulose[38] indicate that the viscometrically estimated decrease of chain length that occurs during the preparation of these samples is accompanied by a corresponding and roughly proportional increase in the number of nonreducing end groups. Similarly, Hess, while being unable to find end groups in undegraded cellulose, has suggested that the number of end groups found in technical celluloses, or in hydro- and oxy-celluloses, is a reliable measure of their degradation.[32] In a more recent work,[39] however,

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[32] K. Hess, D. Grigorescu, E. Steurer, and H. Frahm, *Ber.*, **73B**, 505 (1940).

[33] K. Hess, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 333 (1938).

[34] E. L. Hirst and G. T. Young, *J. Chem. Soc.*, **1938**, 1247.

[35] W. N. Haworth, L. N. Owen, S. Peat, and F. J. Averill, *J. Chem. Soc.*, **1939**, 1885.

[36] W. N. Haworth, R. E. Montanna, and S. Peat, *J. Chem. Soc.*, **1939**, 1899.

[37] H. C. Carrington, W. N. Haworth, E. L. Hirst, and M. Stacey, *J. Chem. Soc.*, **1939** 1901.

[38] G. L. Godman, W. N. Haworth, and S. Peat, *J. Chem. Soc.*, **1939**, 1908.

[39] K. Hess and E. Steurer, *Ber.*, **73B**, 669 (1940).

he has stated that while a decrease in viscometrically determined D.P. is accompanied by a general increase in end groups, there is no simple functional relationship between the two quantities. Thus, samples of equal viscosity produced by different degradative processes (hydrolysis, oxidation, ultraviolet irradiation) may have widely different end-group contents. On the basis of these and other results, Hess has formulated a modification of the chain hypothesis which involves interchain oxygen bridges.

The lack of proportionality between end-group values and D.P.'s as determined by viscosity measurements may be attributed to at least two factors. First, it must be recalled that the type of end groups produced by cleavage depends on the cleavage mechanism. Thus, in hydrolytic breakdown, the production of groups capable of yielding tetramethylglucose seems unambiguous. For certain types of oxidative cleavage, on the other hand, this is very likely not the case. Thus an oxycellulose and a hydrocellulose of equal viscometrically estimated molecular weights could easily have different end-group contents.

Secondly, it must be considered that the end groups and viscosity methods measure different quantities, namely, weight-average and number-average molecular weights. The ratio of these two quantities is a function of chain-length distribution for any sample, and there is no *a priori* or experimental reason for believing that the distribution of chain lengths will be the same for samples subjected to different degradative processes.[40] Thus, the end groups and viscosity methods need not give proportional results for samples degraded by different methods.

The methods described above for the estimation of nonreducing end groups suffer from two obvious disadvantages; on the one hand, the procedures require a long series of rather severe treatments which may easily degrade the original material, and, on the other, they require the isolation of a material which is present in only minute proportions. The difficulties are clearly shown by the large and consistent differences that exist between the schools of Hess and Haworth. For relatively degraded materials, however, the difficulties are much less severe, and the data indicate that this type of end-group method should be capable of giving a reliable relative estimate of the chain length, at least for celluloses of the same general type.

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[40] EDITOR'S NOTE: If all chain linkages were equally available for degradation, the same distribution of chain lengths would result regardless of the method of degradation; there is, however, abundant evidence that, for degradations carried out on fibrous material, different portions of the fiber will vary in their relative rates of degradation according to the method of degradation employed.

The foregoing discussion has dealt only with reducing end groups of the hemiacetal type, and nonreducing end groups capable of forming tetramethylglucose. It has been pointed out, however, that for oxidized celluloses, the latter type of group may be altered so as to render it incapable of forming tetramethylglucose. It appears that, in addition to these types of groups, cellulose chains may under special circumstances contain acidic end groups, which are presumably carboxyl groups formed by oxidation of the hemiacetal end. Thus, cotton purified by the American Chemical Society procedure has been found to contain no free aldehydic reducing groups,[16] but does contain a number of acidic groups corresponding to an equivalent weight of about 100,000. Since the acidic groups of cellulose are considered in Section G of this chapter, they will not be discussed further here.

D. CHEMICAL SIGNIFICANCE OF POLYMOLECULARITY

CLIFFORD B. PURVES

1. Early Work on the Polymolecularity of Cellulose

One of the observations that impressed the earlier investigators was the incomplete solubility of cellulose in caustic soda, and of cellulose ethers and esters in appropriate organic solvents. Not only was solution often partial but the amount dissolved varied between apparently identical samples in a capricious and unpredictable way. Conversely, when a nonsolvent was added in stages to a solution of cellulose or of a derivative, the successive fractions that were precipitated differed markedly among themselves in solubility and other physical properties but often appeared to be identical in chemical respects.[1]

Berl and Klaye[2] were probably the first to note that cellulose nitrates prepared from oxidized or partly hydrolyzed cottons gave less viscous solutions than those derived from undegraded cotton. Similar observations by Ost,[3] made with cuprammonium solutions of degraded celluloses, supported Berl and Klaye's opinion that cellulose existed in many molecular sizes and that the viscosity of its solutions increased with the molecular size. When cellulose esters and ethers were fractionally precipitated with solvents, or were fractionally extracted by them, the less-soluble fractions had higher molecular weights, by osmotic pressure methods, than the more-soluble ones,[4–9] which gave lower viscosities[1, 7, 10, 11] and sometimes passed to a limited extent through ultrafilters.[4, 10] The establishment of the linear

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[1] J. G. McNally and A. P. Godbout, *J. Am. Chem. Soc.*, **51**, 3095 (1929).
[2] E. Berl and R. Klaye, *Z. ges. Schiess- u. Sprengstoffw.*, **2**, 381 (1907).
[3] H. Ost, *Z. angew. Chem.*, **24**, 1892 (1911).
[4] J. Duclaux and E. Wollman, *Bull. soc. chim.*, [4], **27**, 414 (1920).
[5] R. O. Herzog and A. Deripasko, *Cellulosechem.*, **13**, 25 (1932).
[6] I. Okamura, *Cellulosechem.*, **14**, 135 (1933).
[7] H. J. Rocha, *Kolloidchem. Beihefte*, **30**, 230 (1929).
[8] A. J. Medwedew, *Kunststoffe*, **23**, 249 (1933).
[9] R. O. Herzog, *Trans. Faraday Soc.*, **29**, 57 (1933).
[10] W. Kumichel, *Kolloidchem. Beihefte*, **26**, 161 (1928).
[11] I. Sakurada and M. Taniguchi, *J. Soc. Chem. Ind. Japan*, **35**, B249, B253 (1932).

structure for cellulose made it plausible to interpret these and other results as indicating that the individual macromolecules differed in the number of glucose residues they contained or in their degree of polymerization (D.P.). Cellulose, like several other colloids, is a polymolecular material and its individual macromolecules form a polymer-homologous series.[12] Other terms sometimes used in the same sense are polydispersity and heterogeneity. The former is more appropriate for associated colloids like soaps rather than for macromolecular ones. The latter is suitable for systems containing two or more phases.[13, 14]

2. Number-Average and Weight-Average Molecular Weights

Since the molecular chains in a sample of cellulose or its derivatives differ in length, estimations of the molecular weight, or degree of polymerization, give values that are merely averages. The available means of measuring molecular weights include analyses for end groups (see Section C of this chapter), determination of viscosity as developed by Staudinger,[15] perfection of osmotic pressure measurements, mainly by Schulz,[16] and the ultracentrifuge technique of Svedberg.[17] When the same, carefully fractionated specimens are examined both by the osmotic pressure and by the viscosity methods, the results usually agree to within about 10%[18, 19] but wide divergencies are frequent with the more commonly encountered, unfractionated samples. Almost simultaneous reviews of the situation by several authorities focused attention on the exact meaning of the "average" molecular weight obtained by different experimental methods with polymolecular substances.[20, 21, 22]

The classical molecular-weight determinations are derived from the laws

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[12] H. Staudinger, *Ber.*, **59B,** 3019 (1926).

[13] G. V. Schulz, *Z. Elektrochem.*, **44,** 102 (1938).

[14] H. Staudinger, *Melliand Textilber.*, **20,** 781 (1939), reviewed the origin of the concept of polymolecularity.

[15] H. Staudinger, *Die hochmolekularen organischen Verbindungen.* J. Springer, Berlin, 1932.

[16] G. V. Schulz, *Z. physik. Chem.*, **A158,** 237 (1932).

[17] T. Svedberg and K. O. Pedersen, *The Ultracentrifuge.* Clarendon Press, Oxford, 1940.

[18] H. Staudinger and G. V. Schulz, *Ber.*, **68B,** 2320 (1935).

[19] H. Staudinger and H. Freudenberger, *Ber.*, **63B,** 2331 (1930).

[20] W. Kern, *Ber.*, **68B,** 1439 (1935).

[21] E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39,** 153 (1935).

[22] G. V. Schulz, *Z. physik. Chem.*, **B30,** 379 (1935). This article concerns polymolecularity originating in linear polymerizations.

of dilute solutions and, in effect, measure some quantity, such as the depression of the freezing point, the osmotic pressure, or the elevation of the boiling point, that is proportional to the *number* of solute molecules in the quantity of substance weighed out for the experiment. Division of this weight by the number found, or by some factor proportional thereto, then gives the molecular weight, which in the case of cellulose will be very large. Division of the latter weight by the molecular weight of the repeating chemical unit of the chain (basal unit, *Grundmol*) determines the degree of polymerization. Let it be imagined that the polymer-homologous mixture of different chain lengths described in the first two columns of Table 1

TABLE 1

NUMBER-AVERAGE AND WEIGHT-AVERAGE DEGREES OF POLYMERIZATION

Amount, W in g.	D.P.	W/D.P.			$W \times$ D.P.	
10	200	10/200	or 150/3000		2,000	
20	500	20/500	120/3000	= 330/3000	10,000	= 32,000
20	1000	20/1000	60/3000		20,000	
30	2000	30/2000	45/3000		60,000	
				= 65/3000		= 120,000
20	3000	20/3000	20/3000		60,000	
100 g.			395/3000	$= \Sigma[W/\text{D.P.}]$	152,000	$= \Sigma[W \times \text{D.P.}]$

Number-average D.P. = 100/[395/3000] or 760.
Weight-average D.P. = 152,000/100 or 1520.

is weighed out and is submitted to any one of these determinations. The effect produced by the first constituent will be proportional to the number of molecules, each of D.P. 200, present in 10 g. This constituent, for example, will produce an osmotic pressure proportional to 10/200. If W is the total weight in grams of any single constituent in the mixture, the combined effect produced by all the components is proportional to $\Sigma[W/\text{D.P.}]$ and the "average" degree of polymerization is $\Sigma W/\Sigma[W/\text{D.P.}]$, or 760. This kind of average is called the *number-average*. Consideration shows that if the fraction of the anhydroglucose units at one or the other end of all the cellulose chains is determined by one of the chemical end-group methods, the reciprocal of this fraction also gives the number-average degree of polymerization. A similar average would be obtained if the number of individual particles in a definite weight of a heterogeneous dust were counted under a microscope.

Newer methods of determining molecular weight depend not upon the

number of molecules present in a given amount of substance but rather upon the *mass, size, or shape of the individual units*. Each electrically charged atom or molecule flying across the void in an Aston mass spectrograph is deflected by the transverse magnetic field to an extent proportional to its individual mass and independent of the behavior of other particles. The same individual attributes of a dissolved molecule determine its rate of diffusion through a membrane, the Staudinger viscosity of its solution, and its rate of sedimentation in an ultracentrifuge. With linear colloids, the shape may be regarded as a constant, and both Staudinger viscosities and ultracentrifuge data are proportional to the mass, or to the length, of the individual molecule, that is, to the molecular weight or to the degree of polymerization. The effect produced in both of these methods by the first component of the mixture (Table 1) is therefore proportional to g. $\times$ D.P. or to 2000, and the total effect is $\Sigma[W \times \text{D.P.}]$, leading to a *weight-average* degree of polymerization of $\Sigma[W \times \text{D.P.}]/\Sigma W$, or 1520. The only means available to determine weight-averages in an absolute way is with the ultracentrifuge. This technique also gives a third kind of average, defined by the quantity $\frac{\Sigma[W \times (\text{D.P.})^2]}{\Sigma[W \times \text{D.P.}]}$ and called the "Z"-, or the "C"-average.[23, 24] Approximate number-average values and the ratio of molecular length to molecular cross section (shape factors) can usually be calculated from the "Z"-average. Since the operation of an ultracentrifuge still ranks as a specialized profession, the great majority of weight-average determinations are at present derived from Staudinger viscosity data, which are usually calibrated, directly or indirectly, from the ultracentrifuge.[25]

3. The Inadequacies of Number-Average Molecular Weights

The sums of the first three entries in Columns 4 and 6 of Table 1 give the contributions made in number and weight averages, respectively, by the less highly polymerized half of the mixture. This half is responsible for 330/3000 of the total of 395/3000 units, or for 84% of those recorded by a number-average method of estimating molecular weight. On the other hand, the same half of the sample contributes only 32,000/152,000, or 21%, of the total effect produced in a weight-average determination. Since number-average methods are therefore heavily biased in favor of the low-molecular constituents, the degree of polymerization they register will

[23] W. D. Lansing and E. O. Kraemer, *J. Am. Chem. Soc.*, **57**, 1369 (1935).
[24] E. O. Kraemer, *J. Franklin Inst.*, **231**, 1 (1941).
[25] E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

always be less than the corresponding weight-averages when the sample is polymolecular. The discrepancy may amount to 100%, as shown in Table 1, and, for a statistical distribution of chain lengths, the exact relationship has been calculated to be:

$$\frac{\text{number-average D.P.}}{\text{weight-average D.P.}} = \frac{p}{p+1}$$

where p = the fraction of the possible chain linkages which are present in the sample.[26] Since the tensile strength and other valuable physical properties of linear colloids are much more closely connected with the length, or mass, of the macromolecules than with their number, the number-average provides much less practical information than the weight-average degree of polymerization. Consideration of Table 1 also shows that both averages are quite independently obtained from an exact knowledge of the composition of the mixture (Columns 1 and 2) and that the one cannot be calculated from the other without this information. The determination of a number-average, therefore, does little more than set a lower limit to the possible value of the much more significant weight-average.

Another limitation of number-average methods is their insensitivity in the high-molecular range. Sakurada and Okamura[27] have calculated that the entirely random cleavage of about 2.8 glycosidic bonds in a dissolved linear macromolecule will reduce the average chain length, and hence the Staudinger viscosity of the solution, by one-half. If the original substance was cellulose with a degree of polymerization 3000, as it often is in native cotton, the number of molecules in a given weight would be about 1/3000 of the number observed with glucose in similar circumstances, and the anhydroglucose unit at an end of the chain would be in a similar proportion to the whole. The scission of 2.8 bonds in 3000 would increase this fraction to about 4/3000. Both fractions are so minute that the difference between them is below the limits of accuracy of such measurements as osmotic pressure, the determination of reducing end groups by hypoiodite titration or by copper reduction, or the determination of nonreducing end groups by the tetramethylglucose or the periodate method. Failure to recognize the unsuitability of these number-average estimations in the high-molecular field has filled the earlier literature on cellulose with erroneous claims that one treatment or another produced no degradation at all. By way of contrast, it may be mentioned that weight-average methods, such as determinations of sedimentation using the ultracentrifuge

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[26] P. J. Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936).

[27] I. Sakurada and S. Okamura, *Z. physik. Chem.*, **A187**, 289 (1940).

or of viscosity, are sensitive toward amounts of chemical change so minute that they would otherwise pass unnoticed. The spectacular effect of atmospheric oxidation in depressing the viscosity of cellulose dissolved in cuprammonium has been emphasized for years, particularly by Staudinger, who recently found that oxidation by 64 g. of oxygen may reduce the viscosity of half a ton of cotton by about 50%.[28] On this basis, the accidental inclusion of 0.05 cc. of air in an ordinary-scale determination of viscosity in cuprammonium will have an effect of like magnitude and will ruin the estimation. When care is taken to avoid such accidents, viscosity determinations become powerful, reliable tools with which to follow chemical degradations too small to be directly measured. The aging of alkali cellulose by atmospheric oxidation, the acetolysis of cellulose during acetylation, and many other processes can readily be controlled in this way.

A third difficulty with number-average methods lies in their marked response to the adventitious impurities frequently associated with cellulose and pulps. The small osmotic pressure developed by solutions of cellulose derivatives must be carefully distinguished from those, perhaps of comparable magnitude, that are simultaneously produced by traces of ash or other low-molecular substances. Small amounts of oxycelluloses or other readily oxidizable impurities render the copper number, hypoiodite titration, and other determinations of reducing end groups fallaciously high. On the other hand, the ease with which the carbonyl group is chemically changed may render estimations based upon it too low. Rath and Rademacher[29] recently illustrated this point by boiling a pulp in 0.2 to 0.5% aqueous solutions of sodium carbonate. The original copper number of 0.792 decreased by 0.290 to 0.654 units in various experiments. Heating with sodium carbonate solutions under pressure, or with 5% caustic soda at atmospheric pressure, gave copper numbers ranging down to 0.036. Any number-average degree of polymerization that is based on the reducing end of the cellulose macromolecule is therefore very susceptible to errors introduced by the chemical pretreatment, oxidative, alkaline or otherwise, undergone by the sample.

4. The Degree of Polymolecularity[30]

It is often convenient to plot the composition of the mixture described

[28] H. Staudinger and I. Jurisch, *Ber.*, **71B**, 2283 (1938), reviewed the literature dealing with the susceptibility of cellulose toward oxidation.

[29] H. Rath and H. Rademacher, *Melliand Textilber.*, **20**, 749 (1939).

[30] H. Mark, *Paper Trade J.*, **113**, 34 (July 17, 1941), wrote one of the most recent reviews in English.

in Table 1, Columns 1 and 2, as shown in Figures 1 and 2, which are self-explanatory. These data, however, form a highly idealized representation of polymolecularity as it exists in fact. It is extremely unlikely that any chemical process, analytic or synthetic, by which linear colloids are broken down or built up will result in a group of chain lengths, of D.P. 200 for example, to the exclusion of those at least somewhat longer or somewhat

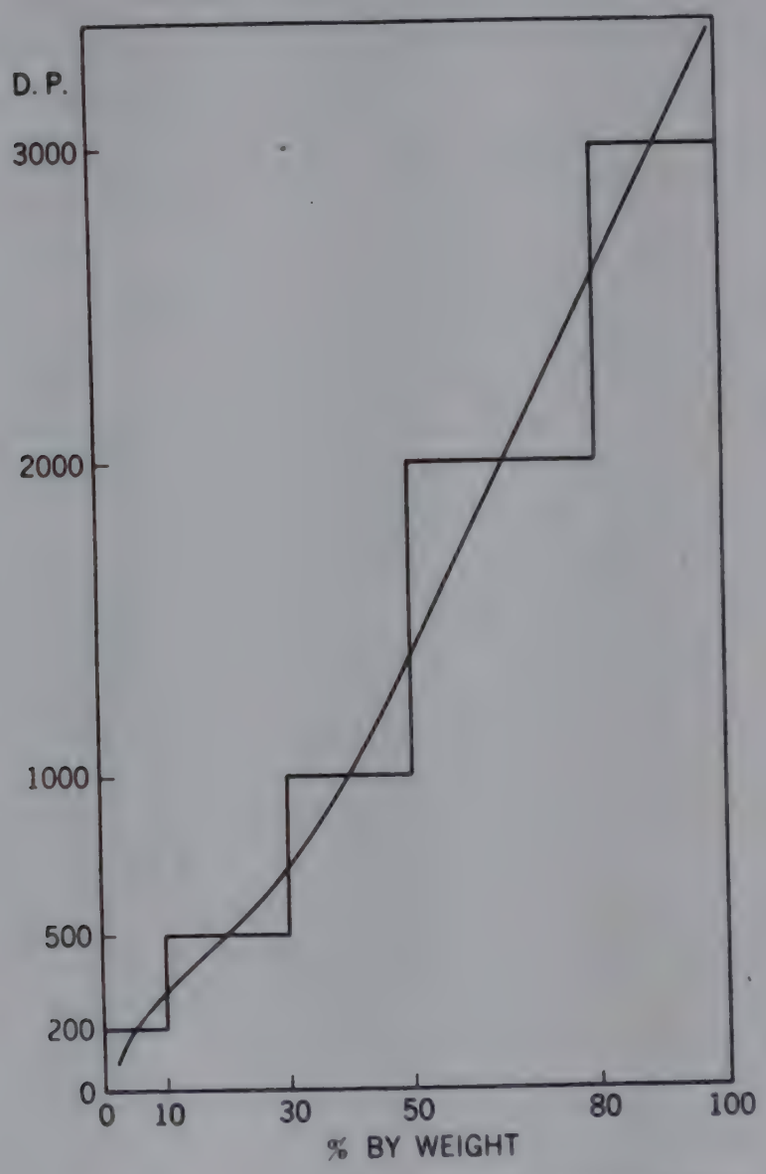

FIG. 1.—INTEGRAL WEIGHT DISTRIBUTION PLOT OF MIXTURE IN TABLE 1.

shorter. The chemical structure of the individual members of a polymer-homologous series is so similar that the separation of one member from the next must depend on quantitative differences in physical properties such as solubility, which in turn are closely connected with the ratio of molecular weights. Cellotetrose was satisfactorily crystallized from its mixture with cellotriose and cellopentose because the difference of ±25% in the molecu

lar weights produced sufficiently distinct solubilities. The separation of chain members of D.P. 200 from those of D.P. 199 and 201, depending on a difference of ±0.5% in molecular weight, seems to be quite out of the question. From every point of view, it is justifiable to regard polymolecularity as a continuous and not as a discontinuous function, since in all but the shortest chains the discontinuities caused by a few glucose units more or less are negligible in comparison to the total chain lengths. The polymolecularity is therefore conveniently expressed by drawing the best smooth curve through the "steps" in Figure 1, or through the points in Figure 2. Differential and integral expressions can then replace the summations already described for the number- and weight-average D.P. When this is done,

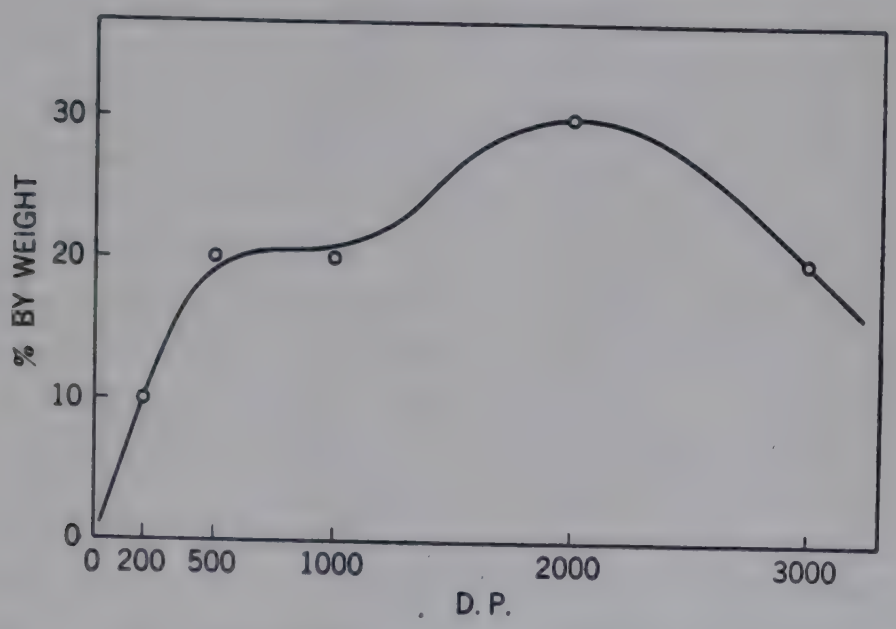

FIG. 2.—DISTRIBUTION PLOT OF MIXTURE IN TABLE 1.

he area under the *integral weight distribution curve* (Fig. 1), given by $\int_0^{100}$ D.P. × d(%), is seen to equal 100 times the weight-average molecular veight. The first differential with respect to D.P. at each point, when olotted against the corresponding D.P., determines the *differential weight-verage distribution* plot.

The determination of either the number- or the weight-average degree of olymerization is obviously insufficient to fix the shape of the plots defining the polymolecularity. A knowledge of both is also inadequate, as nay be illustrated by the fact that a 59% : 41% mixture of macromolecules f D.P. 500 and 3000, respectively, has practically the same number- and veight-averages as the mixture described in Table 1. Independent data re required to determine the distribution of chain lengths, even when the

average degrees of polymerization are known. The problem of procuring these data has been energetically studied during the past few years, especially since it became probable that the nature of the polymolecularity in cellulose products has a marked influence on their physical properties (see Chapter IX, D). Kraemer and Lansing,[21] as well as Signer and Gross,[31] have shown that the shape of the polymolecularity plot may be deduced from ultracentrifuge data and this is probably the most accurate, but by no means the most convenient, method at present available. When it is assumed that the sample is the result of a partial, perfectly random scission of long chains and includes the whole of the original material, mathematical treatments based on Kuhn's reasoning (see Section I of this chapter) provide the distribution of chain lengths at each stage of the degradation.[27, 32–35] Such a mathematical procedure is of course valid only when the underlying assumption is true. The third and most convenient method of investigating polymolecularity is to dissolve the whole of the sample in a chemically inert solvent and to precipitate successive fractions by the stepwise addition of a nonsolvent, or by stepwise changes in temperature. Successive extractions of the original sample by liquids of increasing solvent power produce a similar fractionation. Although the ultracentrifuge or further fractionation shows that the individual fractions are still nonuniform in chain length, no great error is introduced by ignoring any polymolecularity they may possess. Dostal and Mark, indeed, have suggested that allowance be made for this error by calculations based upon the number- and weight-averages of the individual fractions.[36] The determination of their separate degrees of polymerization, by viscosity, osmotic pressure or otherwise, then makes it possible to construct a table similar to Table 1 and to plot the polymolecularity curves. Suitable solvent systems are readily available for many cellulose nitrates,[37] esters,[38] and ethers,[39, 40, 41] but it is

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[31] R. Signer and H. Gross, *Helv. Chim. Acta*, **17**, 726 (1934).

[32] H. Mark and R. Simha, *Trans. Faraday Soc.*, **36**, 611 (1940). Theory and experiment checked quite well for the partial degradation of a cellulose acetate in a homogeneous system.

[33] E. W. Montroll and R. Simha, *J. Chem. Phys.*, **8**, 721 (1940).

[34] R. Simha, *J. Applied Physics*, **12**, 569 (1941).

[35] G. V. Schulz and H. J. Löhmann, *J. prakt. Chem.*, **157**, 238 (1941).

[36] H. Dostal and H. Mark, *Trans. Faraday Soc.*, **33**, 350 (1937).

[37] H. M. Spurlin, *Ind. Eng. Chem.*, **30**, 538 (1938).

[38] A. Dobry, *Bull. soc. chim.*, [5], **2**, 1882 (1935).

[39] L. Clément, C. Rivière, and A. Honnelaitre, *Bull. soc. chim.*, [5], **2**, 707 (1935).

[40] G. Abel and K. Hess, *Cellulosechem.*, **16**, 78 (1935).

[41] S. Glückmann, *Kolloid-Z.*, **76**, 84 (1936).

necessary to make sure in each case that the fractionation does not tend to separate the constituents of the sample according to their degree of chemical substitution as well as according to their D.P. Several instances of this nature are recorded in the literature.[42, 43, 44]

The discovery of a reliable method of fractionating unsubstituted celluloses and pulps has been a matter of greater difficulty because the obvious solvents, such as cuprammonium and concentrated mineral acids like phosphoric acid, all produce some degradation. Since the fractionations are frequently time-consuming and involve numerous separations of solutions from precipitates, the early experiments with these solvents were not very satisfactory.[45] Straus and Levy[46] have recently shown, however, that aqueous solutions of ethylenediamine saturated with cupric hydroxide are good solvents for cellulose. Degradation of the solutions by atmospheric oxidation is so slight that hours elapse before it reveals itself by an appreciable fall in viscosity. The stepwise addition of sulfuric acid to the cupridiamine solution precipitates successive fractions of cellulose, whose weight-average degree of polymerization is in excellent agreement with that determined from the viscosity of the original sample. It is possible that similar fractionations could be carried out in one of the quaternary ammonium bases, such as Triton F (dibenzyldimethylammonium hydroxide) with equally encouraging results. Lachs, Kronman, and their collaborators[47, 48] acetylated pulps with acetic anhydride and zinc chloride and fractionally precipitated the soluble acetates. Although they used mild conditions in order to reduce the degradation occasioned by the catalyst to a minimum, degradation was present and diminished the value of their data, at least as far as the original pulps were concerned. Most of the recent fractionations of pulps are based on the observation that cellulose can be nitrated and renitrated without appreciable degradation, provided that the catalyst in the nitration is not sulfuric acid but a mixture of phosphoric acid and phosphoric anhydride.[49] The polymolecularity of the nitrates (N, about 12.5%) is probably a faithful reflection of that of the original cellulose, but the denitration of the individual fractions has not been ac-

[42] E. Berl and O. Hefter, *Cellulosechem.*, **14**, 65 (1933).
[43] S. Rogowin and S. Glasman, *Kolloid-Z.*, **76**, 210 (1936).
[44] R. Signer and J. Liechti, *Helv. Chim. Acta*, **21**, 530 (1938).
[45] H. Tydén, *Svensk Kem. Tid.*, **51**, 100 (1939); *Chem. Abstracts*, **33**, 6587 (1939).
[46] F. L. Straus and R. M. Levy, *Paper Trade J.*, **114**, 31 (Jan. 15, 1942); **114**, 33 (Apr. 30, 1942).
[47] H. Lachs, J. Kronman, and J. Wajs, *Kolloid-Z.*, **79**, 91 (1937); **84**, 199 (1938).
[48] H. Lachs, J. Kronman, and I. Żurawicki, *Kolloid-Z.*, **87**, 195 (1939).
[49] H. Staudinger and R. Mohr, *Ber.*, **70B**, 2296 (1937).

complished without degradation. The nitration technique is therefore an analytical but not a preparative method.

It has been several years since Staudinger and Feuerstein[50] used viscosities in cuprammonium to determine the average degree of polymerization in numerous celluloses, pulps, and rayons of industrial importance Dolmetsch and Reinecke,[51] Dörr,[52] Jurisch,[53] Schieber,[54] and others have recently extended the data to the determination of the polymolecularities by the nitration method, with special regard to conditions at intermediate stages of the viscose process. Cotton in the unopened boll is stated to have a fairly uniform degree of polymerization in the region of 5000, corresponding to the very large molecular weight of about 800,000 for individual macromolecules. When the boll opens, degradation caused by weathering soon reduces the average D.P. to about 3500, with fractions in the ranges 4200 and 1800. Even the best technical purifications lowered the average D.P. to about 3000.[52, 53] Pulps could be prepared from woods and grasses by the caustic soda process so that the degree of homogeneity and of polymerization remained high. Those prepared by the sulfite method had a lower D.P., about 1000, and the scatter of chain lengths about this average was very considerable. The acid conditions prevalent during sulfite pulping therefore produced quite appreciable degradation.[52, 53, 54] Polymolecularity in rayons, which usually have an average D.P. of 250 to 350,[55] varied quite extensively with the nature of the original pulps and with the details of their manufacture.

5. The Significance of the Alkali-Solubles

It has been known for a long time that celluloses of high viscosity and high tensile strength are only slightly soluble in aqueous alkali and that the portion dissolved contributed least to these desirable physical properties. With a given cellulose, the amount extracted varied widely with the particular alkali used and with the concentration and temperature of the solution. These circumstances induced various industries and trade associations to specify rigid experimental conditions for the determination of the

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[50] H. Staudinger and K. Feuerstein, *Ann.*, **526**, 72 (1936).

[51] H. Dolmetsch and F. Reinecke, *Zellwolle u. Deut. Kunstseiden-Ztg.*, **5**, 219, 299 (1939); *Chem. Abstracts*, **34**, 1167 (1940).

[52] R. E. Dörr, *Angew. Chem.*, **53**, 13 (1940).

[53] I. Jurisch, *Chem.-Ztg.*, **64**, 269 (1940).

[54] W. Schieber, *Angew. Chem.*, **52**, 561 (1939); *Zellwolle u. Deut. Kunstseiden-Ztg.*, **5**, 266 (1939); *Chem. Abstracts*, **34**, 1181 (1940).

[55] H. Staudinger and I. Jurisch, *Melliand Textilber.*, **20**, 693 (1939).

alkali-solubles. The best known variant of these procedures is Cross and Bevan's estimation of *alpha-cellulose*, which is arbitrarily defined as the percentage of the sample that fails to dissolve in 17.5% caustic soda at 20°C. When the alkaline extract is neutralized, the fraction precipitated is denoted by the term *beta-cellulose* and that which still remains in solution is *gamma-cellulose*. The latter includes cellulose chains ranging in length[50] up to about D.P. 10, and those in the beta-cellulose fraction have a D.P.[52] increasing to about 140 to 200. It follows that the insoluble alpha-cellulose consists predominantly of macromolecules of D.P. 200 and more. Since Staudinger and others[56] have repeatedly shown that an average degree of polymerization in this same range is the minimum compatible with the existence of coherent cellulose films and fibers, the alpha-cellulose determination discriminates with a fair degree of accuracy between that part of a pulp which contributes to the tensile strength and that part which makes no direct contribution. It is important to note that the estimation provides no information at all concerning the polymolecularity among the longer chains and therefore suffers in an extreme degree from the limitations in a number-average determination of the degree of polymerization. On the other hand, the alpha-cellulose procedure has the great advantage of fractionating the sample at the polymerization range of critical importance for most purposes.

As already mentioned, the macromolecules in cotton textiles are so long that usually very little, and never more than 15%, of the sample is soluble in alkali.[52] The average degree of polymerization in rayons is comparatively low (D.P. 250 to 350), and at low temperatures rayons dissolve very extensively in 8 to 12% caustic soda. This difference in solubility is the basis of a method for distinguishing cottons from rayons.[57] Neumann, Obogi, and Rogowin[58] fractionally precipitated the dissolved material by stepwise increases in temperature, and Eisenhut[59] showed that the viscosities of caustic soda and cuprammonium solutions are similar. These observations amount to an attractive new method of investigating the polymolecularity of rayons and other degraded celluloses.

The solubility of the shorter cellulose molecules in alkali is not only of analytical interest but also affords a means of reducing the polymolecularity produced by chemical degradations. When used as a pulping agent, caustic soda eliminates the acidity that is a major cause of degradation and simul-

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[56] H. Staudinger and F. Reinecke, *Melliand Textilber.*, **20**, 109 (1939).

[57] O. Eisenhut, *Melliand Textilber.*, **20**, 625 (1939).

[58] R. Neumann, R. Obogi, and S. Rogowin, *Cellulosechem.*, **17**, 87 (1936).

[59] O. Eisenhut, *Cellulosechem.*, **19**, 45 (1941); *Chem. Abstracts*, **36**, 3959 (1942).

taneously extracts most of the shorter chains. The polymolecularity of less uniform pulps, such as those from the sulfite process or from grasses, can be reduced by extracting the shorter chains with cold alkali, and the alpha-cellulose content of the residual pulp rises in consequence. The aging of alkali cellulose in the viscose process, by atmospheric oxidation, is a highly heterogeneous reaction that results in products consisting of molecules of widely varying length. If the degradation is carried out with chlorine acting on pulps suspended in much caustic soda, the action of the oxidant is more uniform throughout the mass, the shorter chain fragments dissolve in the alkali, and the polymolecularity of the product is less than in the former case.[52]

E. NATURE OF THE ASSOCIATION BETWEEN CARBOHYDRATE AND LIGNIN IN WOOD

CLIFFORD B. PURVES

After soluble adsorbed substances have been removed from wood flour or other finely divided plant material by extraction with suitable inert solvents, the residue consists almost entirely of cellulose, hemicelluloses, and lignin. The removal of the latter by alternate extractions with aqueous chlorine dioxide and aqueous pyridine,[1, 2] or, much more conveniently, by alternate chlorinations and extractions with alcohol-pyridine,[3, 4] leaves the *Skelettsubstanzen* or the *holocellulose* in practically quantitative yield. The problem now to be discussed is whether the lignin was originally mixed in an intimate physical way with the holocellulose or was chemically combined with one or more of its constituents.

Although much remains to be discovered concerning the chemical structure of lignin, the great majority of investigators, with the notable exception of Hilpert and his collaborators,[5] are agreed that the basal carbon skeleton is that of phenylpropane (Chapter V). Both phenolic and aliphatic hydroxyl groups are present and a variable proportion of them are methylated. Lignin isolated from plants is supposed to consist of basal units of this general type condensed to amorphous resins of varying solubility and varying molecular weight. It has been suggested[6, 7] that the lignins may be constitutionally related to the much better characterized, crystalline lignans.

Numerous x-ray studies have shown that the cellulose macromolecules in wood are for the most part crystallized against each other to form submicroscopic crystallites in which the dimensions of the unit cell are 10.3 ×

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[1] E. Schmidt, K. Meinel, and E. Zintl, *Ber.*, **60B,** 503 (1927).

[2] E. Schmidt, Y. Tang, and W. Jandebeur, *Cellulosechem.*, **12,** 201 (1931).

[3] G. J. Ritter and E. F. Kurth, *Ind. Eng. Chem.*, **25,** 1250 (1933).

[4] W. G. Van Beckum and G. J. Ritter, *Paper Trade J.*, **108,** 27 (Feb. 16, 1939).

[5] R. S. Hilpert, W. Krüger, and G. Hechler, *Ber.*, **72B,** 1075 (1939); and many other articles by Hilpert.

[6] H. Erdtman, *Ann.*, **516,** 162 (1935).

[7] R. D. Haworth, *Nature*, **147,** 255 (1941).

7.9 × 8.35 Ångstrom units (Chapter III, A). This unit cell is so small that the introduction of even a single oxygenated phenylpropane nucleus would probably crowd it to the point of distortion and more than one would be quite out of the question. The same argument also eliminates hemicelluloses, with the possible exception of xylan,[8] from the interior of the crystallites. Both lignin and hemicelluloses are therefore relegated to the submicroscopic system of faults and fissures present in the regions of the cell wall where the cellulose macromolecules are in random arrangement. Any chemical combination between cellulose and lignin is consequently restricted to occasional unions on the enormous surface that the former develops. There is much more opportunity for combination between lignin and hemicellulose because both are concentrated in the pores of the cellulose mass.

The first clear light upon the nature of this combination was contributed by Brauns[9, 10] who showed that ethanol, used at room temperature, extracted up to 10% of the lignin in sprucewood meal. Since extensive chemical studies showed that the material extracted had the typical chemical properties of lignins and since the conditions of the extraction were chemically inert, Brauns considered that this small fraction of the total lignin existed in a free state in the wood. He called it "native lignin." The failure of the remaining 90% of the lignin to be extracted in the same conditions may be attributed to chemical combination with other wood constituents or to an insolubility caused by a high molecular weight. The latter alternative now appears somewhat unlikely because Hechtman[11] found that native lignin scarcely volatilizes at 290°C. and a pressure of 1 μ when heated in a molecular still. This lignin is therefore of high molecular weight itself but nevertheless it is soluble in alcohol.

The customary methods for removing most, or all, of the lignin from plant materials involve the use of strong acids, cuprammonium hydroxide, or acetolysis at room temperature, or of more dilute solutions of acids and alkalies at elevated temperatures. These reagents are of an hydrolytic nature and the necessity for using them has been taken as an indication that the bulk of the lignin is originally combined with one or more constituents of the holocellulose. On the other hand, it is hardly probable that the fact of such a combination will ever be proved or disproved by such methods because several of them are now definitely known to produce

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[8] W. T. Astbury, R. D. Preston, and A. G. Norman, *Nature*, **136**, 391 (1935).

[9] F. E. Brauns, *J. Am. Chem. Soc.*, **61**, 2120 (1939).

[10] F. E. Brauns, *Paper Trade J.*, **111**, 33 (Oct. 3, 1940).

[11] J. F. Hechtman, *Paper Trade J.*, **114**, 45 (May 28, 1942).

bscure and probably deep-seated changes in the lignin itself.[9] Hot, 10% ydrochloric acid[12] partly converts α-ethoxypropiovanillone, a derivative f one of the lignin building stones, into dark, insoluble resins. The parent ubstance, α-hydroxypropiovanillone, behaved in a similar way when eated with ethanolic hydrogen chloride,[13] which, on the contrary, had a epolymerizing action on isolated lignin.[14] It follows that the molecular eights (1000 to 10,000), the two-[15] or three-[16, 17, 18] dimensional structures, nd the physical properties usually assigned to lignins isolated by such ethods cannot be attributed without further investigation to lignin *n situ*. Products extracted by dioxane[19] or ethanol[20, 21] and hydrogen hloride, or by cuprammonium[22] under very mild conditions, are soluble nough in water to suggest that their molecular complexity is much less han was formerly thought probable.

Lignin can also be extracted by aqueous solutions of butanol and similar lcohols provided the temperature is 120°C. or more.[23] The recovery from spen was 100%, and Bailey[24] inferred that in this case all of the lignin as originally in a free condition. In the case of pine, 20% of the lignin as considered to be chemically combined because it resisted extraction nless 2% of caustic soda was added to the butanol-water. This attempt o discriminate between free and combined lignin, however, involves the ssumption that the aqueous alcohol, buffered to *p*H 7 at room tempera- ure, is still an inert solvent at 120 to 160°C. A similar remark applies to he use of concentrated, aqueous solutions of sodium *p*-cymenesulfonate at 05 to 145°C., which also extract much lignin.[25]

[12] K. Freudenberg, H. Richtzenhain, E. Flickinger, and K. Engler, *Ber.*, **72B**, 1805 1939).

[13] K. A. West, W. L. Hawkins, and H. Hibbert, *J. Am. Chem. Soc.*, **63**, 3038 (1941).

[14] W. B. Hewson, J. L. McCarthy, and H. Hibbert, *J. Am. Chem. Soc.*, **63**, 3041 1941).

[15] E. Wedekind and J. R. Katz, *Ber.*, **62B**, 1172 (1929).

[16] H. Staudinger and E. Dreher, *Ber.*, **69B**, 1729 (1936).

[17] D. L. Loughborough and A. J. Stamm, *J. Phys. Chem.*, **40**, 1113 (1936); **45**, 1137 1941). The former article reviews earlier work.

[18] W. P. Conner, *J. Chem. Physics*, **9**, 591 (1941).

[19] N. I. Nikitin and I. M. Orlowa, *Ber.*, **69B**, 2434 (1936).

[20] J. H. Fisher, W. L. Hawkins, and H. Hibbert, *J. Am. Chem. Soc.*, **63**, 3031 (1941).

[21] H. Hibbert, *Paper Trade J.*, **113**, 35 (July 24, 1941). This article reviewed the hemistry of lignin.

[22] N. I. Nikitin, M. Awidon, and I. M. Orlowa, *Ber.*, **69B**, 2439 (1936).

[23] S. I. Aronovsky and R. A. Gortner, *Ind. Eng. Chem.*, **28**, 1270 (1936).

[24] A. J. Bailey, *Paper Trade J.*, **110**, 29 (Jan. 4, 1940); N. Y. Charbonnier, *Paper Trade J.*, **114**, 31 (Mar. 12, 1942), could not confirm Bailey's results.

[25] Pelipetz, Thesis, Columbia University, 1937; quoted from Hibbert, refs. 20 and 21.

Another approach to the relationship between lignin and carbohydrates in wood was made by Harris, Sherrard, and Mitchell,[26] who methylated maplewood with dimethyl sulfate and caustic soda. Although the concentration of alkali was ample for the methylation of the isolated lignin, that recovered from the methylated wood was unchanged in methoxyl content. The lignin was methylated *in situ*, however, when the wood was first subjected to a mild hydrolysis with 1% acid. These observations very strongly suggested that combination with other constituents of the maplewood masked all lignin hydroxyl groups and that the latter were liberated by the hydrolysis. This combination also appeared to stabilize the enolic form of the carbonyl group supposed to be in lignin, because the lignin in wood absorbed about 50% more chlorine than isolated lignin, which on this assumption exists in the keto form. Brauns[9] came to the opposite conclusion regarding the enolization of the lignin in sprucewood because in this case the methoxyl content was increased by prolonged treatment of the wood with diazomethane.

If it be assumed that lignin-carbohydrate chemical bonds exist, speculation concerning their possible nature is interesting. The hydroxyl groups that both these classes of substances contain might produce ether linkages which, however, would probably be far too stable to be cleaved by the less drastic procedures that actually isolate lignin. Bonds of the ordinary acetal type, between lignin keto and carbohydrate hydroxyl groups, also appear to be improbable because such bonds are usually stable to alkali, which frequently extracts much lignin from plant material in mild conditions. Glycosides engaging aliphatic hydroxyl groups in the lignin are unlikely for similar reasons. On the other hand, glycosides of phenolic and enolic hydroxyl groups are less stable toward acids, are often hydrolyzed by alkali[27] and might undergo a glycoside interchange with the solvent during mild alcoholysis.[28]

The nature of the holocellulose constituent that is supposed to be combined with the lignin is also a matter of doubt. Norman and Shrikhande[29] found that sodium sulfite solution failed to remove much hemicellulose from wood unless the lignin was altered by a previous chlorination that isolated hemicellulose was acidic in nature while wood was not, and

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[26] E. E. Harris, E. C. Sherrard, and R. L. Mitchell, *J. Am. Chem. Soc.*, **56,** 889 (1934).

[27] H. Gehman, L. C. Kreider, and W. L. Evans, *J. Am. Chem. Soc.*, **58,** 2388 (1936).

[28] W. Voss and W. Wachs, *Ann.*, **522,** 240 (1936).

[29] A. G. Norman and J. G. Shrikhande, *Biochem. J.*, **29,** 2258 (1935); see also A. G. Norman, *The Biochemistry of Cellulose, the Polyuronides, Lignin, Etc.* Clarendon Press, Oxford, 1937, pp. 59–63.

hat after isolation the hemicellulose was partly soluble in water. These bservations suggested that the hemicellulose was not isolated in a chemi-ally unchanged condition, and it was natural to suggest that originally it was combined in some way with the lignin. Holmberg and Jahn[30] de-cided that the pentosans and lignin were closely associated in Northern pinewood because the removal of the last few per cent of the latter, by the chlorine dioxide-monoethanolamine method, brought about the simultane-ous removal of much pentosan. Bailey,[24] on the contrary, observed that 20% of pine lignin remained *in situ* after aqueous butanol had extracted the remainder of the lignin and all of the pentosan. Combination with the latter could certainly not be invoked to explain the insolubility of one-fifth of the former, which Bailey considers was bound to the cellulose. Ploetz[31] had a different approach to the problem and obtained very inter-esting results. The digestive juices of the Weinberg snail (*Helix pomatia*) were known to contain the enzymes cellulase, lichenase, and cellobiase, and the purified solutions were capable of reducing cellulose to a water-soluble condition. Mature woods, composed of dead cells, were resistant to the enzymes, which rapidly dissolved much material from the living cells of the pith and cambial layer. Regenerated cellulose and holocellulose were also solubilized with ease. Ploetz inferred that the relatively great resist-ance of the carbohydrates in mature wood was caused either by mechani-cal factors or by the protection afforded by combination with the lignin. In his more recent work, finely divided lindenwood was exhaustively extracted with cupri-ethylenediamine solution, and the extract was acidified. Both the residual wood (34%) and the precipitate from the acidified ex-tract (41%) were readily attacked by the enzyme preparations, but in each case the action became very slow or stopped when the weight ratio of carbohydrate to lignin in the undissolved residues was 1:1. Although these residues partly dissolved when the cupri-diamine and enzyme treat-ments were repeated, the remainders still had a carbohydrate-lignin ratio of unity and contained no pentosan. A rather similar result was obtained by Smith and Purves,[32] who fractionated suitably ground cottonseed hulls into various particle sizes by purely mechanical methods. The finest fractions contained up to 10% of the original lignin associated with an equal weight of carbohydrate which included a relatively large amount of the hemicellulose uronic acids (Chapter IV) and little or no pentosan. It would be imprudent, however, to stress the similarity in the lignin content

[30] C. V. Holmberg and E. C. Jahn, *Paper Trade J.*, **111**, 33 (July 4, 1940).

[31] T. Ploetz, *Ber.*, **73B**, 57, 61, 74, 790 (1940).

[32] M. A. Smith and C. B. Purves, *Ind. Eng. Chem., Anal. Ed.*, **13**, 157 (1941).

of the linden and the cottonseed-hull concentrates because the homogeneity of neither preparation was proved. Moreover, the lignin in the linden may have been altered by the cupri-diamine treatment and the relationship of cottonseed-hull lignin to others is still obscure.

When so much is doubtful, any attempt at a summary must be of a subjective rather than an objective nature. With this proviso, it seems to the author that the following changes may occur in the plant cell and may overlap each other in point of time. During the period when the cell is actively growing, hydroxylated phenylpropane units are elaborated in the sap, possibly in connection with the oxidation-reduction respiratory mechanisms visualized by Hibbert.[20, 33] These phenolic molecules become conjugated in the well-known biochemical fashion with reducing end groups of uronic acid substances of rather low molecular weight, and the slightly methoxylated complexes become intimately absorbed in the porous cellulose wall of the cell.[34] As the latter matures and dies, many of the glycosidic linkages are hydrolyzed, the degree of methoxylation increases,[35] and the rather simple phenylpropane residues tend to condense with each other to form carbohydrate-free resins of unknown and variable molecular weight. Although lignins isolated by chemical methods from the higher plants display a far-reaching analytical similarity to each other,[36] the molecular weight and the ratio of free to combined lignin in the plants themselves may vary, not only with the individual species, but also with its age and condition.[37]

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[33] H. Hibbert, *J. Am. Chem. Soc.*, **61**, 725 (1939).

[34] H. Wislicenus and H. Hempel, *Cellulosechem.*, **14**, 149 (1934).

[35] M. Phillips, M. J. Goss, B. L. Davis, and H. Stevens, *J. Agr. Research*, **59**, 319 (1939).

[36] E. E. Harris, *J. Am. Chem. Soc.*, **58**, 894 (1936).

[37] K. Freudenberg, *Annual Review of Biochemistry*. Vol. 8, Annual Reviews, California, 1939, p. 90.

F. INFLUENCE OF HEMICELLULOSES IN PULPS

CLIFFORD B. PURVES

1. Nature of Hemicelluloses Remaining in Cellulose after Pulping

It has already been mentioned (Section E of this chapter) that alternate chlorinations and extractions with alcohol-pyridine remove all lignin but no substantial amount of carbohydrate from plant tissue.[1] The product (holocellulose) therefore contains not only all the cellulose but also all of the arabans, fructosans, galactans, polyuronides, xylans, mannans, and other "polyoses" comprised in the hemicellulose[2] fraction of the original cell (Chapter IV). Some of these substances, particularly the first four, become at least partly soluble in water after the lignin has been removed. All are soluble, or partly soluble, in aqueous alkali and most are hydrolyzed more readily than cellulose by dilute acid. Mitchell and Ritter[3] have determined the percentage solubility of holocellulose in such conditions. Any pulping method that involves extractions with aqueous acid or alkali will produce, not holocellulose, but a residue consisting of the cellulose plus those portions of the hemicellulose that the particular agent has failed to dissolve.

Well-known pulping procedures that fall in this category include Cross and Bevan's alternate chlorinations and extractions with hot, aqueous sodium sulfite,[4, 5] Norman and Jenkins' use of alkaline hypochlorite,[6] and Kürschner and Hoffer's[7] alcoholic-nitric acid technique. The pulps obtained from uniform plant samples by these and other methods will naturally differ among themselves in the amount and composition of the

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[1] W. G. Van Beckum and G. J. Ritter, *Paper Trade J.*, **104**, 49 (May 13, 1937).

[2] E. Schulze, *Ber.*, **24**, 2277 (1891).

[3] R. L. Mitchell and G. J. Ritter, *J. Am. Chem. Soc.*, **62**, 1958 (1940).

[4] C. F. Cross and E. J. Bevan, *Cellulose*. Longmans, Green & Co., London, 1895, p. 95.

[5] E. F. Kurth and G. J. Ritter, *J. Am. Chem. Soc.*, **56**, 2720 (1934).

[6] A. G. Norman and S. H. Jenkins, *Biochem. J.*, **27**, 818 (1933).

[7] K. Kürschner and A. Hoffer, *Chem.-Ztg.*, **55**, 161, 182 (1931). This article gives comparative data with many other methods.

hemicellulose that remains with the cellulose. The difference will also extend to the degree of degradation produced in both these constituents. Ritter and his collaborators[5, 8] showed that a partial hydrolysis of spruce holocellulose, for thirty minutes with 1% sulfuric acid, left a pulp closely similar in composition to the Cross and Bevan cellulose from the same wood but of lower viscosity in cuprammonium. According to Reid and Lynch,[9] pulps obtained by the Cross and Bevan and the Norman and Jenkins methods have approximately the same composition, but the more drastic conditions of the alcoholic-nitric acid procedure give products in lower yield and of lower viscosity. Pulps prepared by the large-scale technical methods described in Chapter VI will differ among themselves in similar ways, even when derived from the same lot of wood.

Any really thorough investigation of the hemicellulose content of pulps must commence with the identification and the estimation of the sugar residues, other than glucose, that are present. The pulp, or an extracted fraction thereof, is hydrolyzed by aqueous acid to a mixture of reducing monosaccharides and of uronic acids which is then examined by the methods of sugar chemistry.[10, 11] Although interest in this tedious task has revived among investigators of pulps in recent years,[5, 12] most analyses are still restricted to the determination of the total pentosan and uronic acid content of the material. These estimations are carried out by distilling the sample with 12% hydrochloric acid, whereupon the uronic acids evolve a quantitative yield of carbon dioxide and a nonquantitative but reproducible amount of furfural. Pentosans also evolve the latter under the same circumstances, the yield being reproducible but nonquantitative and dependent upon the particular pentose sugar forming the basal unit of the polysaccharide. Although these factors render the pentosan estimation inaccurate when the pentose is unknown, the difficulty is not serious in the case of pulps from hardwoods (deciduous) or from many straws because the overwhelming mass of the residual hemicellulose can be assumed to be of the xylan-glucuronide type.[13] The same remark applies to the pentosan determination with softwood (coniferous) pulps, in which an hexosan (man-

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[8] W. G. Van Beckum and G. J. Ritter, *Paper Trade J.*, **108**, 27 (Feb. 16, 1939).

[9] J. D. Reid and D. F. J. Lynch, *Ind. Eng. Chem., Anal. Ed.*, **9**, 570 (1937).

[10] A. W. van der Haar, *Anleitung zum Nachweis zur Trennung und Bestimmung der Monosaccharide und Aldehydsäuren*. Bornträger, Berlin, 1920.

[11] K. Hess, *Die Chemie der Zellulose*. Akademische Verlagsgesellschaft m. b. H., Leipzig, 1928, pp. 104–129.

[12] See, for example, R. E. Dörr, *Angew. Chem.*, **53**, 292 (1940).

[13] A. G. Norman, *The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.* Clarendon Press, Oxford, 1937, Appendix, pp. 211–223.

nan) replaces much of the xylan.[14] In such cases, the percentage content of "cellulose" in the pulp can be corrected for "pentosan" or for uronic acid.

(*a*) *Alkali-Soluble Hemicelluloses*

Since the hemicelluloses are extensively soluble in alkali, a large portion of those contained in a pulp will pass into solution during the Cross and Bevan determination of alpha-cellulose, or during any similar determination of the alkali-solubles. The Cross and Bevan beta- and gamma-cellulose fractions will accordingly contain variable amounts of polysaccharides based on sugars other than glucose. Mitchell and Ritter[3] estimated the average degree of polymerization of the water-soluble, and the 4% caustic soda-soluble, fractions of maple holocellulose. The hypoiodite titration of reducing end groups plus uronic acid estimations gave approximate values of 7 to 13 and of about 75, respectively, for the degree of polymerization (D.P.). The presence of such comparatively small molecules in pulps will produce relatively large osmotic pressures, and large effects in procedures connected with the end groups, such as iodine or copper numbers, but the influence on viscosity and ultracentrifuge determinations will be small.

In brief, these hemicellulose units will decrease the observed number-average degree of polymerization much more than the weight-average and therefore increase the polymolecularity in the manner already outlined for short cellulose molecules (Section D of this chapter). In spite of the presence of short hemicellulose chains, the cuprammonium viscosity of holocellulose pulp is high[15] and the brief, mild chlorination required in its preparation failed to degrade the cellulose portion in a substantial way. Since the undegraded hemicelluloses have apparent chain lengths of 150–160 (see below), the values of 7 to 73 quoted above show that the same mild conditions were quite sufficient to cause extensive degradation in the hemicellulose fraction of holocellulose. This inference is in agreement with the work of Stamm and Cohen,[16] who found that the rate of hydrolysis of hemicellulose-containing pulps in concentrated phosphoric acid was distinctly higher than that of cotton cellulose in the same conditions. Campbell and Bamford[17] showed that boiling 1% sulfuric acid hydrolyzed woods more extensively when their pentosan content was high, although

[14] A. W. Schorger, *Ind. Eng. Chem.*, **9**, 748 (1917).
[15] W. G. Van Beckum and G. J. Ritter, *Paper Trade J.*, **109**, 107 (Nov. 30, 1939).
[16] A. J. Stamm and W. E. Cohen, *J. Phys. Chem.*, **42**, 921 (1938).
[17] W. G. Campbell and K. F. Bamford, *J. Soc. Chem. Ind.*, **58**, 180T (1939).

it is true that this evidence was obscured by the possible effect of the wood lignins. Finally, Hawley and Fleck[18] suggested that a standard, partial hydrolysis with aqueous acid might estimate the low-molecular, readily hydrolyzed, less useful part of Cross and Bevan wood pulps.

(*b*) *Alkali-Insoluble Hemicelluloses*

Although much hemicellulose is extracted by alkali, it has been shown repeatedly that some of the xylan in straws and hardwoods, and some of the mannan in softwoods, remains in the alpha-cellulose. These alkali-resistant fractions have been named "cellulosans"[19] because their association with the cellulose is supposed to correspond to the relationship between the components of a solid solution or a mixed crystal.[20] Since the alpha-cellulose determination in itself gives no information about these cellulosans, it is necessary to estimate xylan and mannan individually. The former, of course, is readily determined as furfural, but the mannan estimation requires the acid hydrolysis of the pulp and the isolation of mannose, usually as the crystalline, sparingly soluble phenylhydrazone.[21–25] By careful extractions of straws or beechwood with caustic soda in a nitrogen atmosphere, with and without the restricted action of 0.25% aqueous chlorine dioxide, Husemann[26] was able to isolate some of each xylan in a practically undegraded condition. When solutions of the xylans, and of their methyl, methylacetyl, and benzoylacetyl derivatives, were examined by the osmotic pressure and the Staudinger viscosity methods, the macromolecules were found to have a chain length of 150 and a linear configuration. A slight degree of branching was not excluded and would reconcile the data with the chain length of 19–20 assigned to xylans by the methylated end group and the hypoiodite method.[27] Fractional precipitation studies showed that xylan is the first polysaccharide to have no significant amount of polymolecularity and to have a uniform degree of polymeriza-

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[18] L. F. Hawley and L. C. Fleck, *Ind. Eng. Chem.*, **19**, 850 (1927).
[19] L. F. Hawley and A. G. Norman, *Ind. Eng. Chem.*, **24**, 1190 (1932).
[20] W. T. Astbury, R. D. Preston, and A. G. Norman, *Nature*, **136**, 391 (1935).
[21] E. Bourquelot and H. Hérissey, *Compt. rend.*, **129**, 339 (1899).
[22] G. Bertrand, *Compt. rend.*, **129**, 1025 (1899).
[23] A. W. Schorger, *Ind. Eng. Chem.*, **9**, 556 (1917).
[24] W. H. Dore, *Ind. Eng. Chem.*, **12**, 476 (1920).
[25] E. Hägglund and L. C. Bratt, *Svensk Kem. Tid.*, **48**, 125 (1936); *Papier-Fabr.*, **34** Tech.-wiss. Tl., 100 (1936); *Chem. Abstracts*, **30**, 7333 (1936).
[26] E. Husemann, *J. prakt. Chem.*, **155**, 13 (1940).
[27] R. A. S. Bywater, W. N. Haworth, E. L. Hirst, and S. Peat, *J. Chem. Soc.*, 1937 1983.

tion. Since this is the case, it seems justifiable to assume a D.P. of 150 for undegraded "cellulosan" xylan, which Husemann did not examine. Parallel work by the same author with undegraded, extracted spruce mannan suggested that the molecule is linear[28] and that the chain length is uniform at D.P. 160. This mannan was isolated in two main fractions that agreed in viscosity but differed in solubility, optical rotation, and methoxyl content[28] (OCH_3, 0.55 to 0.92% and 1.0 to 3.0%, respectively).

2. Effect of Hemicelluloses on Cellulose Uses

In Section D of this chapter, evidence was outlined to demonstrate that cellulose molecules of less than D.P. 200 form powdery aggregates and are incapable of producing coherent films and fibers. Husemann's chain-length data make it plain that any xylan or mannan in cellulose products is quite unlikely to contribute in any direct way to the tensile strength, particularly when the effects of degradation during pulping and purification are remembered. Heuser and Schorsch[29] and Dörr[12] found that neither xylan nor mannan gives true viscose solutions when shaken with caustic soda and carbon disulfide. These hemicelluloses run through the viscose process, although some or all of the xylan can be eliminated by difficult filtrations, and are present in the finished film or rayon, to which they impart an increased solubility in alkali and a decreased resistance toward dilute acid. Husemann[26] also prepared undegraded acetates of xylan and mannan by acetylation with acetic anhydride and pyridine. The triacetylmannan was soluble in chloroform[30] and meta-cresol and presumably would cause no difficulty in the production of acetate films and rayons. Both undegraded diacetylxylan and the degraded product prepared with acidic acetylation catalysts[31] were insoluble or difficultly soluble in chloroform, meta-cresol, and acetone. These acetylated xylans are therefore liable to produce complications in the filtration of cellulose acetate solutions. Husemann's nitrates of xylan and mannan were both insoluble in acetone and butyl acetate, and their presence in pyroxylins and guncottons is undesirable for this and other reasons.[32] Naiman and Troitsky[33]

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[28] Ivory nut mannan also occurs in two fractions and the molecule is linear. F. Klages, *Ann.*, **509**, 159 (1934); **512**, 185 (1934).

[29] E. Heuser and G. Schorsch, *Cellulosechem.*, **9**, 93 (1928).

[30] Compare J. Patterson, *J. Chem. Soc.*, **123**, 1139 (1923).

[31] E. Heuser and P. Schlosser, *Ber.*, **56B**, 392 (1923).

[32] B. Rassow and E. Dörr, *J. prakt. Chem.*, **108**, 113 (1924).

[33] I. M. Naiman and N. D. Troitsky, *J. Soc. Chem. Ind.*, **54**, 255T (1935). This article includes a literature review.

and others[32] have shown that the hydrolytic and oxidative action of technical nitrating conditions is sufficient to remove most or all of the xylan from the pulp, particularly when the water content of the nitrating mixture is considerable. The presence of the pentosan in such cases reveals itself in an increased consumption of the nitrating reagent. Even a brief outline of the possible disadvantages of wood or straw pulps as chemical raw materials, however, can hardly be concluded without the remark that they can now be prepared to contain little or no xylan and very little mannan. This desirable result has been achieved by careful attention to colloidal conditions (as avoidance of drying-out) during the successive steps of pulping, bleaching, and skilful extractions with alkali[12, 34] or, possibly, with dilute acid.[35]

Several recent investigations[36–40] have shown beyond doubt that the presence of hemicelluloses is almost essential in pulps destined for paper. They appear to improve the colloidal properties that the fibers develop during the mechanical "beating" process and to increase the physical strength of the final paper. The tendency of isolated hemicelluloses to dry from the water-wet state as tough, horny masses may possibly be connected with this behavior, and, incidentally, may also explain the occasional unreactivity of wood pulps during acetylation or other chemical processes. Hemicelluloses may also modify the physical condition of pulps and papers in another way when uronic acids are present, because the carboxyl groups that the latter contain will alter the acid-base exchange characteristics. This matter is discussed in the following section.

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[34] F. Olsen, *Ind. Eng. Chem.*, **30**, 524 (1938).

[35] A. Nowotnowna, *Biochem. J.*, **30**, 2177 (1936).

[36] H. E. Obermanns, *Paper Trade J.*, **103**, 83 (Aug. 13, 1936). A literature review is included.

[37] H. H. Houtz and E. F. Kurth, *Paper Trade J.*, **109**, 38 (Dec. 14, 1939).

[38] G. Jayme and G. Schwab, *Papier-Fabr.*, **38**, Tech.-wiss. Tl., 45 (1940); *Chem. Abstracts*, **34**, 7601 (1940).

[39] G. Jayme and E. Kerler, *Holz Roh- u. Werkstoff*, **3**, 2 (1940); *Chem. Abstracts*, **34**, 4900 (1940).

[40] G. J. Hajny and G. J. Ritter, *Paper Trade J.*, **113**, 83 (Sept. 25, 1941). A review is included.

G. BASE-EXCHANGE PROPERTIES

ARNOLD M. SOOKNE AND MILTON HARRIS

It was early observed that neutral salt solutions become acidic when passed through filter paper. Studies of this and related phenomena have shown that they result from the ability of cellulosic materials to engage in cation-exchange reactions which are similar to those that occur in the zeolites; thus, for example, properly activated jute has been shown to be capable of softening water.[1] It has now been clearly established that these exchange reactions are limited to cations,[1, 2, 3] and that cellulosic products exchange metal ions for one another or for hydrogen ions, or hydrogen ions for metal ions with a rapidity that is characteristic of inorganic reactions. Further, the reactions are easily reversed,[1, 4, 5] although it must be pointed out that polyvalent ions (Ca^{++}, Mg^{++}, Fe^{+++}, etc.) are retained by the fibers with greater tenacity than those of the alkali metals.[4, 5, 6]

In naturally occurring cellulosic fibers, the exchange capacity is principally accounted for by the materials associated with the cellulose, such as pectic substances, lignin, etc.,[1, 7] whereas in fibers freed from these substances, this capacity has been accounted for by acidic groups in the cellulose itself.[7, 8] Some evidence has been presented which indicates that these acidic groups are carboxyl groups and that a small but definite number of such groups may be present in the original cellulose. In certain oxycelluloses, however, the proportion of such groups becomes relatively large.

1. Exchange Reactions Involving Replacement of Metallic Cations by Each Other

A thorough investigation of the base-exchange properties of cotton has

[1] D. A. McLean and L. A. Wooten, *Ind. Eng. Chem.*, **31**, 1138 (1939).
[2] P. Pascal and J. Hansot, *Compt. rend.*, **195**, 349 (1932).
[3] J. Gavoret, *Compt. rend.*, **204**, 1643 (1937).
[4] A. C. Walker and M. H. Quell, *J. Textile Inst.*, **24**, T123 (1933).
[5] A. C. Walker and M. H. Quell, *J. Textile Inst.*, **24**, T131 (1933).
[6] H. Rath and H. Dolmetsch, *Z. Textil-Ind. (Klepzig's)*, **41**, 475 (1938).
[7] A. M. Sookne and M. Harris, *J. Research Natl. Bur. Standards*, **25**, 47 (1940); *Am. Dyestuff Reptr.*, **29**, 333 (1940).
[8] S. M. Neale and W. A. Stringfellow, *Trans. Faraday Soc.*, **33**, 881 (1937).

been made by Walker and Quell[4, 5] in which they quantitatively determined the constituents of the ash of cotton before and after washing the fiber with water, acids, and especially dilute salt solutions. On the basis of these studies, it was concluded that in naturally occurring cellulosic materials, the acidic groups appear to exist in the salt form,[9] the cations being, for the most part, polyvalent cations of high affinity. When the fiber in this form is immersed in a salt solution, exchange between the cations on the fiber and those in the solution occurs, the extent of the exchange depending on the relative affinities of the cations for the acidic groups, and on their concentrations. Thus, tightly bound Ca^{++} ions may be replaced by less tightly bound Na^{+} ions, if the latter appear in sufficiently high concentrations. On the other hand, the polyvalent ions Ca^{++} and Mg^{++} were found to be readily interchangeable, simply by washing the fiber with the respective Mg^{++} or Ca^{++} salts. Such exchanges are not accompanied by appreciable changes in the *p*H value of the solution surrounding the fiber.

Rath and Dolmetsch[6] confirmed the fact that alkali cations may be rather easily washed from the fiber, but that polyvalent cations like Ca^{++} adhere tenaciously unless the fiber is washed with acid or a salt solution. These investigators also studied the absorption of Ag^{+} ions by cotton from solutions of silver acetate. The amount of silver absorbed was taken as a measure of the number of carboxyl groups in the material. When applied to native cellulose, the process involves the exchange of Ag^{+} ions in the solution for the metal cations already on the fiber in accordance with the following equation:

$$RCOOM + AgA \rightleftharpoons RCOOAg + MA \qquad (1)$$

(where RCOO— represents the acidic group on the fiber; M, the cations; and AgA, the silver salt used).

If the cellulose exists in the acidic form, then the reaction is:

$$RCOOH + AgA \rightleftharpoons RCOOAg + HA \qquad (2)$$

As has been pointed out elsewhere,[11] however, not all of the carboxyl groups bind silver when the cellulosic material is immersed in a dilute solution of silver acetate. Complete reaction of the carboxyl groups with the Ag^{+} ion is opposed by the competition of metallic cations in (1) and hydrogen ions in (2). These investigators have shown, however, that the

[9] Evidence for this has also been presented by Kolthoff,[10] McLean and Wooten,[1] and Sookne and Harris.[7]

[10] I. M. Kolthoff, *Pharm. Weekblad*, **58**, 233 (1921).

[11] A. M. Sookne and M. Harris, *J. Research Natl. Bur. Standards*, **26**, 205 (1941); *Am. Dyestuff Reptr.*, **30**, 107 (1941).

silver titration method leads to a satisfactory estimate of the number of carboxyl groups if the titration is performed on electrodialyzed cotton (to eliminate competition from metallic cations) using a solution of the silver salt of a very weak acid (to minimize competition from hydrogen ions). Silver *o*-nitrophenolate was found to be a suitable salt.[11]

2. Exchange Reactions Involving Replacement of Metallic Cations by Hydrogen

When the fiber in the salt form is immersed in an acidic solution, exchange of the cations already present by hydrogen ions occurs in an amount that has been shown to be dependent on the mass action law,[7] and the extent of the exchange is directly indicated by the decrease of the hydrogen-ion concentration of the solution. This procedure forms a basis for estimating the number of cations on the fiber, and hence the number of acidic groups. The process is essentially a back-titration of the acidic groups, and offers a method of preparing cellulose in the acidic form. Cellulose in this form can also be prepared electrodialytically.[12] It has been shown, especially by Kolthoff,[10] McLean and Wooten,[1] and Sookne and Harris,[7] that the acid-binding capacity of cellulose is quantitatively determined by its content of bound cationic ash. Neale and Stringfellow[8] early made use of this principle as a means for estimating the acidic groups in various celluloses. Their procedure consisted in immersing a sample of the electrodialyzed fiber in a solution of NaOH and NaCl, and then back-titrating with HCl. The method was applied to various oxycelluloses, and the number of carboxyl groups found was proportional to the amount of oxygen consumed in the preparation of the oxycellulose. The estimated strengths of the carboxyl groups were of the proper order of magnitude for a hydroxycarboxylic acid. However, a carboxyl content of only 0.002 milliequivalent per g. was found for unoxidized standard cloth. This value is much lower than that obtained by other investigators on similar materials. It should be noted that this method is essentially equivalent to titrating the salt form of cellulose with acid, in the presence of a neutral salt, thus:

$$\mathrm{RCOOH + NaOH \rightleftharpoons RCOONa + H_2O}$$

$$\mathrm{RCOONa + \quad HCl \rightleftharpoons RCOOH \quad + NaCl}$$

The method involving titration of the salt form of cellulose with acid has been used by McLean and Wooten[1] and Sookne and Harris.[7] The former

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[12] A. M. Sookne, C. H. Fugitt, and J. Steinhardt, *J. Research Natl. Bur. Standards*, 25, 61 (1940); *Am. Dyestuff Reptr.*, 29, 333 (1940).

were able to show that the acid-binding capacity of a cellulosic material is proportional to the ash content at an arbitrary *p*H value, and that the exchange capacity is associated principally with the noncellulosic concomitants of the material (pectic substances, lignin, etc.). In addition, it was shown that cellulosic materials engage in no anion exchange of appreciable magnitude. The latter, in their study of the cation-exchange properties of cotton, further demonstrated that the cationic ash determines the acid-binding capacity of cotton at any *p*H, and also that most

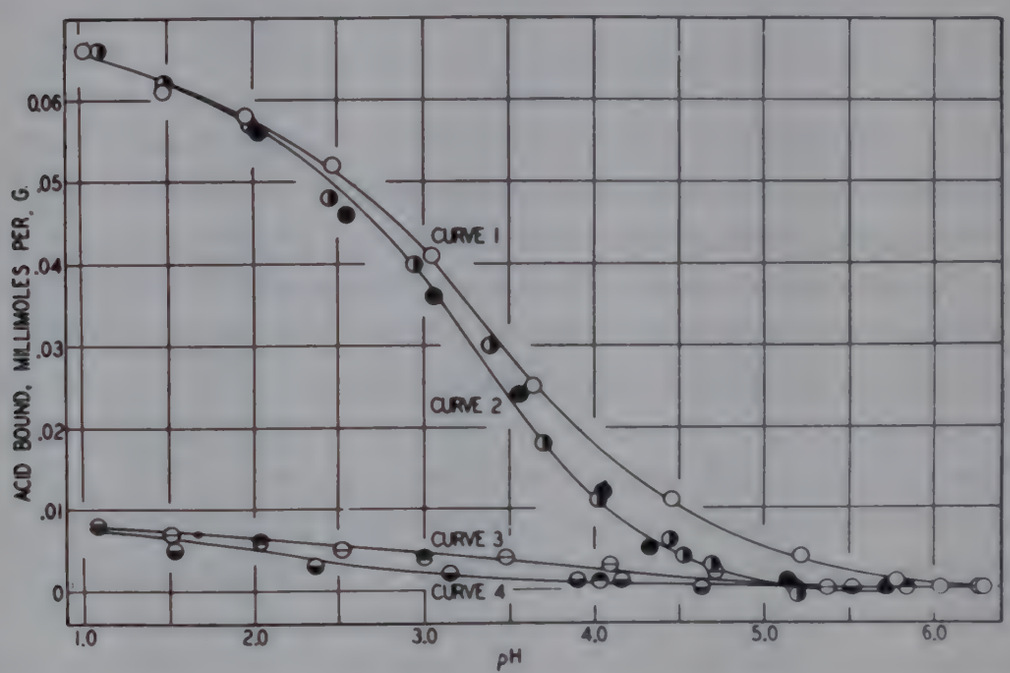

FIG. 3.—COMBINATION OF DEWAXED AND OF LIME-WASHED DEPECTINIZED COTTON WITH HYDROCHLORIC ACID AT 0 °C. (SOOKNE AND HARRIS[7]).

Curve 1, dewaxed cotton in the absence of added salt, ○.

Curve 2, dewaxed cotton in hydrochloric acid-potassium chloride solutions of 0.1 *M* ionic strength, ◑; and in solutions of 1.0 *M* ionic strength, ●.

Curve 3, depectinized cotton in the absence of added salt, ⊖.

Curve 4, depectinized cotton in solutions of 0.1 *M* ionic strength, ◒: and in solutions of 1.0 *M* ionic strength, ⊜.

of the ash is associated with the pectic substance in the raw fiber. The absorption of acid in solutions of any *p*H value was also shown to be consistent with the mass action law and the Donnan equilibrium; that is, cellulose absorbs less acid from a solution containing acid plus salt than from a solution at the same *p*H but containing only acid. From the complete titration curves (see Fig. 3) and the hydrogen-ion equivalence of the ash, the maximum acid bound by different samples of cotton was ascertained, which in turn permitted the quantitative allocation of the acid

bound to the principle constituents of the fiber. Thus, in a sample of raw cotton which had an acid-binding capacity of 0.065 milliequivalent per g., 0.055 milliequivalent was accounted for by the pectic substance, the remainder by acidic groups in the cellulose itself.

A variation of the above method for estimating acidic groups involves engaging these groups with tightly bound cations, such as calcium, followed by electrodialytic determination of the cation content of the sample.[12] There appears to be some question as to whether all the valences of a polyvalent cation are engaged by the fiber. It has been found[11] that the same number of equivalents of calcium, silver, and hydrogen were bound by depectinized cotton, indicating that both valences of the calcium are satisfied by the acidic groups of the fiber. A contrary conclusion, however, has been reached by Rath and Dolmetsch,[6] who found that approximately twice as many equivalents of calcium as of sodium were bound by the same material. This would correspond to the formation of a basic salt or of a mixed salt such as R_{cell}–Ca–Cl.

Schmidt and coworkers[13] used a conductometric method to measure the number of carboxyl groups of various celluloses. Their method consisted of adding a quantity of dilute alkali to electrodialyzed cotton, and then titrating with acid. The number of acidic groups in the sample was estimated by extrapolating the curve relating conductivity of the system to the amount of acid added. With this method, Schmidt obtained a content of carboxyl groups of 0.28% for "native cellulose," the quantity being so constant for variously purified celluloses of widely different types that Schmidt proposed this as a criterion for native cellulose. Neale and Stringfellow were unable to repeat this conductometric titration, their data showing that a smooth conductivity curve, incapable of being extrapolated, is obtained.[8] In addition, Neale and Stringfellow were unable to repeat Schmidt's direct titration of electrodialyzed cotton with NaOH. Unfortunately, Schmidt's papers do not contain any of the experimental curves but only the results of the extrapolations.

3. Exchange Reactions Involving Replacement of Hydrogen Ions by Metallic Cations

As pointed out earlier, cellulose may be obtained in the acidic form by replacement of its cations by hydrogen ions, either by treatment of the fiber with acid or by an electrodialytic process. The acidic groups of

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[13] E. Schmidt, *et al.*, *Cellulosechem.*, **13**, 129 (1932); *Naturwissenschaften*, **21**, 206 (1933); *Ber.*, **67B**, 2037 (1934); **68B**, 542 (1935); **69B**, 366 (1936).

cellulose in this form can be titrated directly and this has also been used for estimation of the acidic groups in cellulose.

Lüdtke[14] attempted to measure the content of acidic groups of rayons and pulps by titrating the cation-freed fiber with dilute alkali in the presence of a large excess of calcium acetate. However, Neale and Stringfellow have indicated that the method is unreliable since there is a large uncertainty in this end point, presumably because of the buffering effect of the acetate.[8] The silver nitrophenolate method,[11] which has been described earlier in this discussion, has been found to work satisfactorily on the acidic form of cotton cellulose and gives values for the content of acidic groups which are in good agreement with those obtained by the back-titration with acid of the salt form of the cellulose.

Addendum

Recent publications[15, 16] on base-exchange are of especial interest for their discussion of the strength of the acidic groups in cellulose and the effect of specific cations on base-exchange.

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[14] M. Lüdtke, *Papier-Fabr.*, **32**, Tech.-wiss. Tl., 509, 528 (1934); *Angew. Chem.*, **48**, 650 (1935); *Biochem. Z.*, **285**, 78 (1936).

[15] E. Heymann and G. Rabinov, *J. Phys. Chem.*, **45**, 1152 (1941); *Trans. Faraday Soc.*, **38**, 209 (1942).

[16] G. Rabinov and E. Heymann, *J. Phys. Chem.*, **45**, 1167 (1941).

H. CELLULOSE TESTS

CLIFFORD B. PURVES

Perhaps the simplest approach to the voluminous literature concerned with the evaluation of cellulose and cellulose pulps is first to describe those tests which estimate the more commonly occurring groups of natural, non-cellulose impurities. Consideration can next be given to the methods by which the qualities of pure cellulose (cotton) can be judged. The ground is then cleared for a description of the additional estimations which the presence of hemicelluloses requires. No systematic attempt will be made to cover specialized tests evolved by the rayon, paper, or other cellulose-using industries, or tests for substances deliberately added during processing. Trade Associations and Government Bureaus in the principal cellulose-producing and cellulose-consuming countries have minute and elaborate directions for the carrying out of the estimations. The differences between these specifications are usually a matter of technical detail rather than of principle. No attempt will be made to catalog these differences here. Attention is also called to the excellent compilation of cellulose tests by Dorée,[1] the existence of which relieves the author of detailed descriptions in many cases.

1. Estimation of Naturally Occurring Inorganic and Low-Molecular-Weight Impurities

(*a*) *Fats, Waxes, and Resin Acids*

These substances are intimately associated with cellulose in its natural state and their removal forms the first step in an accurate chemical examination of the fiber. The finely divided, air-dry material is thoroughly extracted (from 6 to 24 hrs.) in a continuous extractor, usually with hot ethyl ether or with the constant-boiling mixture composed of one volume of ethanol and two volumes of benzene. Since the material extracted is a complex mixture of substances of varying solubility, different solvents

[1] C. Dorée, *The Methods of Cellulose Chemistry.* Van Nostrand, New York, 1933.

often extract different amounts, as in the case of pinewood[2] and cotton.[3]

Quantitative estimations are carried out by reducing a weighed amount (2–10 g.) of the air-dry sample to a physical state that permits easy penetration by the extractant, which may be petroleum ether, ethyl ether, benzene,[3] carbon tetrachloride,[4] methylene dichloride,[5] ethanol, or any other rather low-boiling, chemically stable organic liquid that dissolves fats. A Soxhlet extractor is used and after 6 to 12 hrs., when the process is complete, the extract is evaporated and the residue dried at 100–105°C. for a short time. The weight of the dry residue represents the weight of the organo-soluble (ether-soluble or benzene-soluble, for example) constituents of the sample according to the solvent used.

Sometimes these solubles are heated with half-normal alcoholic caustic soda, and the residue remaining after evaporation is shaken with water. Extraction of the resulting emulsion with petroleum ether separates the nonsaponifiable from the saponifiable constituents that are then present as water-soluble sodium salts.[4] Ordinary raw cottons usually contain 0.4 to 0.7% of ether-solubles, but Arkansas green lint varieties may run as high as 14–17%.[6] The fat and wax contents of prepared pulps are low and variable.

(*b*) *Moisture Content*

Cellulose, like other hygroscopic colloids, absorbs moisture from its environment until an equilibrium is attained, the position of which depends upon the cellulose sample and the temperature. Cotton samples usually contain 6–8% of moisture when kept exposed to air of normal humidity at room temperature. Davidson and Shorter,[7] who subjected the problem of estimating the moisture in cotton to a careful examination, observed that 6- to 8-g. samples could be completely dried in an evacuated desiccator containing phosphorus pentoxide. The weight of the sample decreased during four to six weeks at room temperature to a constant value. This

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[2] E. F. Kurth and E. C. Sherrard, *Ind. Eng. Chem.*, **23**, 1156 (1931).

[3] P. H. Clifford, L. Higginbotham, and R. G. Fargher, *J. Textile Inst.*, **15**, T120 (1924). References to earlier work on cotton are given, and the chemical nature of benzene extractives is described.

[4] Tech. Assoc. Pulp Paper Ind., *Standards*, T 405 m-40; *Paper Trade J.*, **110**, 46 (May 23, 1940).

[5] Faserstoff-Analysenkommission, Merkblatt No. 5, *Papier-Fabr.*, **32**, Tech.-wiss. Tl., 345 (1934).

[6] C. M. Conrad, *Science*, **94**, 113 (1941).

[7] G. F. Davidson and S. A. Shorter, *J. Textile Inst.*, **21**, T165 (1930).

value was called the *true dry weight* because it was independent of the number of times the sample was exposed to moisture and redried in the same manner.

Technically, the moisture content of cellulose is much more conveniently obtained by drying at an elevated temperature, which is usually between 105 and 110°C., for a fixed time or until the weight decreases to a value that remains constant within any arbitrary standard of accuracy that may be considered sufficient. If heated atmospheric air is used for the drying, it is obviously impossible for the sample to lose moisture beyond the equilibrium point set by the relative humidity and the temperature. Davidson and Shorter found that the final weight reached by cotton samples dried at 107°C. in 10% relative humidity was 0.15% more than the true dry weight, or that the samples had retained about 0.15% of moisture. Dry, or almost dry, cellulose competes on nearly equal terms with phosphorus pentoxide for moisture, and much is absorbed even in 1 or 2 min. at room temperature. The final weighing of the sample must therefore be carried out with special precautions. One method, used industrially for large samples, is to obtain the final weight without removing the sample from the hot oven. Quite elaborate pieces of equipment, with automatic temperature control, rotary driers, and built-in analytical balances, have been constructed for this purpose.[8] The difference in temperature of the air in which the initial and final weighings are carried out tends to make the latter slightly low. This small error opposes that caused by any humidity present in the air in the oven, and the final result with cotton is very close to the true dry weight.[9] On the laboratory scale, it is usual to heat 2- to 5-g. samples in an open weighing container and to replace the closely fitting stopper *before* removal from the oven. The closed weighing bottle is quickly transferred to a desiccator and cooled to room temperature. After loosening the stopper for an instant to equalize the air pressure within and without the container, the final weighing is carried out and duplicate determinations should check to 0.1%.[10]

Although the difficulties connected with the hygroscopicity of cellulose are largely avoided in the techniques just described, drying at elevated temperatures must tend to evolve traces of volatile substances from samples containing fatty or resinous impurities. Impurities that are readily decomposed or oxidized may also evolve additional water or other volatile

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[8] K. Göhde, *Papier-Fabr.*, **37**, Tech.-wiss. Tl., 320 (1939); *Chem. Abstracts*, **34**, 4902 (1940).

[9] M. Stephenson, *J. Textile Inst.*, **29**, T297 (1938).

[10] Am. Soc. Testing Materials, *Proceedings*, **38, I**, 1016 (1938).

material by virtue of a chemical breakdown. W. J. Wald and the author, in an unpublished research, prepared Klason lignin from Northern pinewood that had been exhaustively extracted with alcohol-benzene and with water. Drying for 10 hrs. in air at 105°C. reduced the carbon content of the isolated lignin by 3 to 4% and that of the wood by more than 1%,[11] but the analysis of the holocellulose remained unchanged. In the case of woods, therefore, drying in a hot oven may promote very substantial chemical alteration, and lignin-containing pulps may exhibit similar behavior in a minor degree. Pure cotton cellulose is chemically stable for many hours at 110°C. in air.

The error connected with the volatilization of oily materials can be eliminated, and that caused by oxidation can be reduced, by distilling the moisture from the sample with an inert organic liquid which is of suitable boiling point and which is immiscible with water. The distillate separates into an aqueous layer, whose volume can be measured in a graduate, and into the organic liquid layer, which retains any traces of oils. Bidwell and Sterling[12, 13] found that toluene (b. p., 111°C.) gave good results but that xylene (b. p., 137°C.) produced decomposition in some less stable carbohydrates such as fructose. Tetrachloroethylene (b. p., 118.5°C.) has the advantage of being nonflammable.[14]

Mitchell[15] has recently developed a radically new moisture determination which promises to circumvent all the uncertainties of the other procedures. A weight of sample, chosen to contain 50 to 250 mg. of water, is soaked in 100 cc. of dry methanol for 1 hr. and the increase in the water content of the methanol is estimated by titration with the Karl Fischer reagent. This reagent consists of iodine, sulfur dioxide, and pyridine dissolved in methanol[16] and is not likely to be affected by the probable contaminants in the sample. Mitchell's estimation also leaves the specimen in a state suitable for further examination. Samples recovered from methods involving heating may be altered in their chemical or colloidal properties and are usually reserved for the determination of the ash content.

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[11] Compare D. MacDougall and W. A. DeLong, *Can. J. Research*, **20B**, 40 (1942). This article has other references.

[12] G. L. Bidwell and W. F. Sterling, *Ind. Eng. Chem.*, **17**, 147 (1925).

[13] Tech. Assoc. Pulp Paper Ind., *Standards*, T 3 m-34.

[14] A. J. Bailey, *Ind. Eng. Chem., Anal. Ed.*, **9**, 568 (1937).

[15] J. Mitchell, Jr., *Ind. Eng. Chem., Anal. Ed.*, **12**, 390 (1940).

[16] D. M. Smith, W. M. D. Bryant, and J. Mitchell, Jr., *J. Am. Chem. Soc.*, **61**, 2407 (1939).

(c) *Ash*[17, 18]

The sample, 2 to 10 g. (often that recovered from a moisture determination), is weighed into a crucible, which may be of platinum, alundum, porcelain, or silica, although platinum should be avoided if zinc and some other heavy metals are present.[19] A lid is fitted on the crucible and, by preference, the incineration is carried out in a muffle furnace kept at 500 to 600°C. If a burner is used, cautious initial heating of the lid will control the formation of voluminous, tarry decomposition products. The cover may be removed to complete the oxidation of the residual carbon, after which the crucible and contents are cooled in a desiccator and reweighed.

The ash from native celluloses usually contains two or more of the following metals, which are present as oxides, phosphates, or carbonates: sodium, potassium, calcium, magnesium, silicon, and traces of iron, together, occasionally, with traces of several other heavy metals. The ash from the first four of these constituents dissolves in water and produces an alkaline solution. In order to determine the *ash alkalinity*, the entire ash is warmed for 1 hr. with 10 to 15 cc. of 0.01 *N* sulfuric acid, the mixture is diluted to 70 cc. with distilled water, and is titrated to a methyl red end point with 0.01 *N* caustic soda. The result is expressed as cc. of *N* acid required to neutralize the ash from 100 g. of sample or, alternatively, as the amount required for 1 g. of ash.[20] Since the water-soluble oxides and carbonates in the ash were originally present as salts of carboxylic acids, it is easy to understand why the ash alkalinity is closely connected with the number of carboxyl groups in the sample and with its affinity for methylene blue and other basic dyestuffs.[19] (See also Section I, 3 of this chapter.) It is a common observation that the neutral calcium and magnesium salts of polybasic acids are less soluble than the sodium or potassium ones, probably because the dibasic anions form a bridge between two carboxylic groups belonging to different molecules. The sodium salts of pectic acid or of suitably oxidized celluloses, for example, are freely soluble in water but the barium or magnesium salts are insoluble.[21] Such cross linkages between different macromolecules may affect the physical properties of cellulose that depend upon the size of the ultimate physical particle. If,

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[17] Am. Soc. Testing Materials, *Proceedings*, **38, I,** 1024 (1938).

[18] Tech. Assoc. Pulp Paper Ind., *Standards*, T 413 m-39; *Paper Trade J.*, **110,** 28 (May 30, 1940).

[19] B. P. Ridge, M. Corner, and H. S. Cliff, *J. Textile Inst.*, **24,** T293 (1933).

[20] C. Dorée, *The Methods of Cellulose Chemistry*, p. 21; see ref. 1, p. 119.

[21] E. C. Yackel and W. O. Kenyon, *J. Am. Chem. Soc.*, **64,** 121 (1942).

for example, a cellulose ester or ether contains an occasional carboxyl group, cross-linked to another through a dibasic metal, the viscosity observed in a neutral, organic solvent might be substantially enhanced. Decomposition of the salt by dilute acid, or dissociation by diluting the solution, might be expected to reduce the viscosity toward its ash-free value. Effects like these were observed by Rogovin and Schlachover[22] for cellulose nitrate-calcium oxide systems, although they interpreted their data in terms of calcium alcoholates rather than calcium salts.

The neutral, insoluble ash constituents represent for the most part inorganic materials that originally were occluded in the fiber. In addition to diminishing the clarity of solutions of cellulose and its derivatives, these constituents may enter as catalysts into various reactions. One conspicuous example is the efficiency of traces of copper or manganese in catalyzing the oxidative breakdown of rayon textiles, particularly when the rayon is impregnated with rubber. Fabrics destined for the latter process must not contain more than 0.001% of copper or 0.0005% of manganese.[23] Since these minute amounts may readily be acquired from water supplies, metallic equipment, or other chemicals during processing, the detection and estimation of the nonsoluble ash constituents has attracted considerable attention. Micro methods have been developed for copper, zinc, and iron,[19] titanium and iron,[24] and arsenic, lead, and copper.[25] In some of these methods, the organic material in the sample is destroyed by digestion with nitric acid instead of by incineration.

To sum up, the ash constituents of cellulose may modify its properties to an extent altogether out of proportion to their absolute amount, which rarely exceeds a few tenths of 1%.

2. Estimations for "Pure" Celluloses (Cotton, etc.)

(*a*) *Reducing Power*[26]

Alkaline cupric sulfate,[27] alkaline potassium ferricyanide,[28] silver ni-

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[22] S. Rogowin and M. Schlachover, *Kolloid-Z.*, **78**, 224 (1937).

[23] C. A. Seibert, *Am. Dyestuff Reptr.*, **29**, P136 (1940).

[24] J. M. Jarmus and W. R. Willets, *Paper Trade J.*, **98**, 41 (Jan. 4, 1934); **98**, 37 (Jan. 18, 1934).

[25] W. G. Leach, *Analyst*, **66**, 372 (1941).

[26] C. Dorée, *The Methods of Cellulose Chemistry*, pp. 31–44; see ref. 1, p. 119.

[27] C. G. Schwalbe, *Ber.*, **40**, 1347 (1907); *Z. angew. Chem.*, **23**, 924 (1910).

[28] M. Freiberger, *Melliand Textilber.*, **11**, 127 (1930).

trate,[29] and ceric sulfate[30] have been employed in this estimation but the use of the first is the most general. Some modifications of Schwalbe's original method[27] retain tartaric or citric acid salts to keep the copper dissolved in the alkaline solution,[31, 32, 33] but the others follow Braidy[34, 35, 36] in using a sodium carbonate-sodium bicarbonate copper solution which is less sensitive to autoreduction and more sensitive toward the reduction of the sample. Some of the methods estimate all of the copper precipitated on the fiber or remaining in solution by various inorganic procedures[27, 31, 37] and, although often rapid, have to undergo a small, doubtful correction for adsorbed cupric copper. Others redissolve the cuprous oxide in an acidified solution of ferric sulfate,[35] ferric alum,[38] or phosphomolybdic acid[36] and estimate the amount of reduction caused by the cuprous oxide in this solution by titration with standard potassium permanganate[38, 39] or ceric sulfate,[40] or by a colorimetric method.[32] Perhaps the most generally accepted procedure is that of Braidy, as developed by Clibbens and Geake[35] for cottons and by Burton and Rasch[36] for papers. The former modification is briefly reproduced[26]:

The finely divided cotton (2.5 g.) or paper or pulp (1.5 g.) is suddenly covered by an already boiling mixture of 5 cc. of Solution A and 95 cc. of Solution B. The first of these solutions is 10% copper sulfate pentahydrate and the second contains 5% sodium bicarbonate and 35% crystalline sodium carbonate. Air bubbles are eliminated with a glass rod and the flask is kept deeply immersed in a covered water bath for exactly 3 hrs. The cellulose-cupric oxide residue is recovered, well washed with dilute sodium carbonate and hot water, and it is then extracted with 15 to 35 cc. of a solution containing 140 cc. of concentrated sulfuric acid and 100 g. of ferric ammonium sulfate per liter. When all the cuprous oxide has dissolved, the residue is washed with 2 *N* sulfuric acid and the

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[29] K. Götze, *Melliand Textilber.*, **8**, 624, 696 (1927).

[30] R. B. Forster, S. M. Kaji, and K. Venkataraman, *J. Soc. Chem. Ind.*, **57**, 310T (1938).

[31] T. Dokkum, *Mitt. des niederl. Reichfaserforschungsinstituts;* cited by E. Geiger and G. Müller.[32]

[32] E. Geiger and G. Müller, *Helv. Chim. Acta*, **23**, 820 (1940).

[33] H. Wenzl, *Tech. Chem. Papier- u. Zellstoff-Fabr.*, **26**, 109 (1929); *Chem. Abstracts*, **24**, 6004 (1930).

[34] A. Braidy, *Rev. gén. mat. color.*, **25**, 35 (1921).

[35] D. A. Clibbens and A. Geake, *J. Textile Inst.*, **15**, T27 (1924).

[36] J. O. Burton and R. H. Rasch, *Bur. Standards J. Research*, **6**, 603 (1931).

[37] D. Krüger and E. Tschirch, *Zellstoff u. Papier*, **14**, 233 (1934); *Chem. Abstracts* **28**, 5230 (1934).

[38] E. Knecht and L. Thompson, *J. Soc. Dyers Colourists*, **36**, 255 (1920).

[39] E. Hägglund, *Cellulosechem.*, **11**, 1 (1934).

[40] W. A. Richardson, R. S. Higginbotham, and F. D. Farrow, *J. Textile Inst.*, **27**, T131 (1936). This method was developed for starch.

filtrate plus washings is titrated with 0.04 *N* potassium permanganate. The titration is corrected for a small blank. A simple calculation gives the weight of cuprous copper equivalent to the permanganate titration (1 cc. of 0.04 *N* $KMnO_4$ = 2.543 mg. Cu) and the weight in grams corresponding to 100 g. of the cellulose. The latter value, called the *copper number*, is 0.1 or less for undegraded celluloses and may be much higher for rayons and for hydro- and oxy-celluloses. When the copper number exceeds 4 (6 for the smaller pulp or paper sample), the reagents approach the point of exhaustion and a smaller sample weight is taken; this fact is specifically mentioned because the observed copper number is not independent of the sample weight. The Knecht and Thompson procedure[38] is suitable for larger copper numbers.

Heyes[41] adapted the Schwalbe-Braidy method to a semimicro scale with satisfactory results and employed a 0.25-g. sample. Geiger and Müller[32] worked with 0.1- to 10-mg. samples and used colorimetric methods involving α,α'-dipyridyl[42, 43] or *o*-phenanthroline[44, 45] to estimate the iron reduced to the ferrous state. Although this micro method is of potential value for the examination of damaged spots in textiles, sampling difficulties lowered the agreement between duplicates. The micro adaptions of the hypoiodite[46] and the Dokkum[31] methods were less satisfactory.[32] In qualitative work, the deposition of traces of cuprous oxide on the fiber is often hard to observe. Müller[47] overcame this difficulty by steeping the specimen in water and dilute acetic acid until the blue tinge caused by cupric salts had disappeared and the color was orange-red. When the sample was steeped in a dilute solution of silver nitrate in dilute acetic acid, black, easily observed silver oxide was deposited. A similar treatment with very dilute gold chloride caused the fiber to become impregnated with colloidal gold that was deep purple in color.

Many comparisons have been made between the principal macroscale ways of estimating reduction. The Schwalbe-Braidy method was more sensitive than the original Schwalbe[27] and the Knecht and Thompson procedures[35] and was more accurate than the Dokkum,[31] whose advantage lies in its rapidity (only 15 min. instead of 3 hrs. heating).[48] Smit and Peper[49] compared the Dokkum, Braidy, Wenzl,[33] and Hägglund[39] methods

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[41] T. F. Heyes, *J. Soc. Chem. Ind.*, **47**, 90T (1928).

[42] R. Hill, *Proc. Roy. Soc.* (*London*), **B107**, 205 (1930–31).

[43] F. Feigl and M. Hamburg, *Z. anal. Chem.*, **86**, 7 (1931).

[44] A. Thiel, H. Heinrich, and E. Van Hengel, *Ber.*, **71B**, 756 (1938).

[45] G. H. Walden, L. P. Hammett, and R. P. Chapman, *J. Am. Chem. Soc.*, **55**, 2649 (1933).

[46] M. Bergmann and H. Machemer, *Ber.*, **63B**, 316, 2304 (1930).

[47] F. Müller, *Helv. Chim. Acta*, **22**, 376 (1939).

[48] W. Schramek and H. Cristoph, *Kolloid-Beihefte*, **48**, 322 (1938).

[49] R. Smit and J. P. Peper, *Melliand Textilber.*, **15**, 218 (1934).

and found that the first two gave approximately the same copper numbers. Similar work on various methods has been carried out by most of the other investigators cited.

(*b*) *Aldehyde Groups*

The work of Cajori[50] showed that the oxidation of glucose by alkaline hypoiodite is stoichiometric but that the reagent does not affect fructose, a keto sugar. Although the following method, by Harris and his collaborators,[51, 52] estimates the aldehyde groups in hydrocelluloses and in periodate oxycellulose correctly, it has not yet been extensively tested on other types of oxycellulose.

Ten cc. of a 0.05 *M* sodium borate buffer, having a *p*H of 9.2 at 25°C., was mixed in a glass-stoppered Erlenmeyer flask, kept in a thermostat at 25°C., with 20 cc. of a 0.03 *M* iodine solution containing 20 g. of potassium iodide per liter. The sample of periodate oxycellulose, weighing not more that 100 mg., was introduced immediately after mixing and the temperature was maintained at 25°C. for 6 hrs. Acidification with 15 cc. of 0.1 *N* hydrochloric acid was followed by a careful titration of the residual iodine with standard (about 0.013 *N*) sodium thiosulfate solution, using starch as the indicator. The iodine disappearing in a blank run containing no cellulose was subtracted from the result, which was also corrected for the small amount of iodine used, in unknown ways, by the same weight of undegraded cellulose. In the earlier article,[51] it was suggested that the latter correction could also be obtained with a sample of the unknown that had been oxidized in the same conditions with the hypoiodite and had been freed from excess iodine by thorough washing with water. This article also gave conditions for the oxidation of 1-g. samples of hydrocellulose in a 0.2 *M* sodium carbonate-sodium bicarbonate buffer. The iodine normality was 0.05 (100 cc. to 25 cc. of buffer) and the oxidation was complete in less than 6 hrs., either at *p*H 9.2 and 25°C. or at *p*H 10.6 and 0°C. The number of cc. of 0.1 *N* iodine corresponding to a 1-g. sample has been called the *iodine number*.[46] Since the oxidation of one mole of aldehyde group requires 2 liters of *N* iodine, 20,000 divided by the iodine number gives the number-average molecular weight of a hydrocellulose.

(*c*) *Carboxyl Groups*

The acidic groups associated with cellulose are usually present as salts and the modern titrimetric methods of estimation commence by regenerating the free acids. Extraction for an hour or two with cold 0.14 *N*,[53] or

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[50] F. A. Cajori, *J. Biol. Chem.*, **54**, 617 (1922).

[51] A. R. Martin, L. Smith, R. L. Whistler, and M. Harris, *J. Research Natl. Bur. Standards*, **27**, 449 (1941); *Am. Dyestuff Reptr.*, **30**, No. 23, 628 (1941).

[52] H. A. Rutherford, F. W. Minor, A. R. Martin, and M. Harris, *J. Research Natl. Bur. Standards*, **29**, 131 (1942).

[53] M. Lüdtke, *Angew. Chem.*, **48**, 650 (1935).

0.01 *N* hydrochloric acid[54] or, in the case of starch, with 4.5% sulfuric acid,[55] is followed by exhaustive washing with distilled water, sometimes assisted by electrodialysis.[54] Whatever the method, the cationic ash (ash alkalinity) should be reduced to a very low figure of the order of 0.004 milliequivalents per g. The silver *o*-nitrophenolate method outlined below was developed by Sookne and Harris[54] for cottons and was successfully adapted to starches and oxystarches by Elizer[55] who compared it with a copper acetate procedure.

Excess silver oxide was shaken in aqueous *o*-nitrophenol at 70°C. and filtration gave a nearly saturated, approximately 0.01 *N* solution of the phenolate.[54] The same result was obtained by melting the phenol with an equal weight of the oxide and extracting the resulting cake with water. Five grams of cellulose, or 1.5 g. of starch, was immersed in 100 cc. of the silver phenolate solution at room temperature and the mixture was occasionally shaken. The next day the difference in silver content between a 50-cc. aliquot of the supernatant liquor and a blank was determined by the Volhard method[56, 57] and the result was expressed as milliequivalents of silver per g. of sample. The results with starch checked fairly well with similar estimations made with neutral copper acetate.[55]

The silver *o*-nitrophenolate can also be replaced with calcium acetate. Yackel and Kenyon,[21] who studied Lüdtke's original method,[53] let 0.5-g. samples of deashed oxycellulose steep for 2 hrs. at 25°C. in 50 cc. of water and 30 cc. of approximately 0.5 *N* solution. Thirty-cc. aliquots of the supernatant liquor were then titrated to a phenolphthalein end point with 0.1 *N* sodium hydroxide. Although the results were consistent within themselves, they were not altogether so with data by other methods tried[58] and no advantage was gained by increasing the normality of the calcium acetate to 1.0. This observation is at variance with Heymann and Rabinov's[59] remark to the effect that the exchange reaction is not quite complete in 0.5 *N* calcium acetate. Weber,[60] who used neutralized 0.1 *N* barium chloride, made sure of this point by carrying out successive extractions, each of 15 to 20 cc., on the same 0.499 g. of purified, ash-free spruce pulp. On titration to a phenolphthalein end point with 0.01 *N* baryta, the first 80 cc. of extracts were found to consume 2.75 cc., the next 70 cc., 0.25 cc., and the last 50 cc., 0.15 cc. of the baryta. The total of 3.15 cc. was therefore the acidic equivalent of the sample.

Details of the well-known methylene blue absorption test for the acidity of cellulose[61, 62] are to be found in the book by Dorée.[1]

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[54] A. M. Sookne and M. Harris, *J. Research Natl. Bur. Standards*, **26**, 205 (1941).

[55] L. H. Elizer, *Ind. Eng. Chem., Anal. Ed.*, **14**, 635 (1942).

[56] J. Volhard, *J. prakt. Chem.*, **9**, 217 (1874).

[57] W. W. Scott, *Standard Methods of Chemical Analysis*. 5th ed., Vol. 1, Van Nostrand, New York, 1939, p. 824.

[58] C. C. Unruh and W. O. Kenyon, *J. Am. Chem. Soc.*, **64**, 127 (1942).

[59] E. Heymann and G. Rabinov, *Trans. Faraday Soc.*, **38**, 209 (1942).

[60] O. H. Weber, *J. prakt. Chem.*, **158**, 33 (1941). Literature review included.

[61] C. Birtwell, D. A. Clibbens, and B. P. Ridge, *J. Textile Inst.*, **14**, T297 (1923).

[62] D. A. Clibbens and A. Geake, *J. Textile Inst.*, **17**, T127 (1926).

A 0.004 *M* solution of the purified dyestuff hydrochloride is used, often in a buffered solution, and the amount absorbed is found by determining the excess remaining in the supernatant liquor, either colorimetrically or by titration with the acidic dye, naphthol yellow S. Weber[60] appears to have put this semiquantitative method on a quantitative basis by paying attention to the considerations discussed in Section G of this chapter. He used a 0.03 to 0.04% solution of the purest methylene blue and ash-free cellulose samples of 50 to 250 mg., depending upon their acidity. The stock solution of the dye, 5 or 10 cc., was diluted to 100 cc. with distilled water and successive volumes of 10 to 15 cc. were repeatedly allowed to soak through the fiber in a special apparatus. The fiber was then washed with three 1-cc. volumes of water containing a trace of methylene blue, and thereafter the fixed dyestuff was eluted with successive 10- to 15-cc. volumes of 0.01 *N* hydrochloric acid until the last extract was quite colorless. The methylene blue in the combined extracts was determined colorimetrically, preferably with a photometric instrument, and the results agreed to within 1% with those obtained by the barium chloride method.

Another method of estimating acidity was studied by Rebek[63] who let cellulose absorb the colorless, pseudo base of crystal violet from water and several different organic liquids. The absorbed dye was estimated as nitrogen and the method was considered by Weber to be less certain and more tedious than his own.

Considerable attention has been given of late to the estimation of the acidity in papers,[64] which is usually carried out by titrating an extract made with hot, or cold,[65] water. The problem is complicated by the presence of alum, rosin, and other sizes and is important because papers of high acidity seem to deteriorate rapidly on aging.

(*d*) *Alpha-, Beta-, and Gamma-Cellulose*

The estimation of alpha-cellulose was originally proposed in order to assess the behavior of a given pulp during mercerization or during the preparation of alkali cellulose.[66, 67, 68] Ritter[69] and Launer[70] reviewed the considerable literature dealing with the details of the estimation, and the

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[63] M. Rebek, *Kolloid-Z.*, **92**, 217 (1940); cf. D. Krüger and F. Oberlies, *Ber.*, **74B**, 663 (1941).

[64] D. Burton, *Analyst*, **63**, 19 (1938), reviewed the literature.

[65] H. F. Launer, *J. Research Natl. Bur. Standards*, **23**, 663 (1939).

[66] C. F. Cross and E. J. Bevan, *Researches on Cellulose, (1905–1910)*. Longmans, Green, London, pp. 23, 97.

[67] H. Jentgen, *Kunststoffe*, **1**, 161 (1911).

[68] Steudte, *Kunstseide u. Zellwolle*, **21**, 122 (1939); *Chem. Abstracts*, **33**, 4429 (1939).

[69] G. J. Ritter, *Ind. Eng. Chem., Anal. Ed.*, **1**, 52 (1929), Method IV.

[70] H. F. Launer, *J. Research Natl. Bur. Standards*, **18**, 333 (1937); **20**, 87 (1938).

former work forms the basis of the following outline. The method given in Dorée[71] differs in detail only.

The sample of cotton or pulp, of known moisture content and weight about 3 g., is covered, at 20°C., with 35 cc. of carbonate-free sodium hydroxide solution made up to contain 17.5 g. of the base in 100 g. of solution. A total of 40 cc. more of the alkali is added in 10-cc. volumes over a period of 10 min., during which time the mass is occasionally agitated with a glass rod. After a total mercerization time of 45 min., 75 cc. of distilled water is mixed thoroughly into the mass, which is promptly filtered on a Gooch crucible and washed with 750 cc. of distilled water at 25°C. When desired, the filtrate and the wash water are preserved for the beta- and gamma-cellulose estimations. The mat of alpha-cellulose on the Gooch crucible is now soaked for 10 min. in 10% acetic acid to remove adsorbed alkali and is finally washed quite free from acid with distilled water. Drying to constant weight at 105°C. takes at least 6 hrs. and is carried out with the precautions observed during the determination of moisture.

When beta- and gamma-cellulose values are required, exactly one-half of the alkaline liquors from the alpha-cellulose determination is made just acid to methyl orange and, after several hours, the precipitated beta-cellulose is removed by filtration or on the centrifuge. A suitable aliquot of the mother liquor is then cautiously diluted with an equal volume of concentrated sulfuric acid, an excess of 9% potassium dichromate is added, and the gamma-cellulose is completely oxidized by boiling the solution for 5 min. A back titration with 0.5 *M* ferrous ammonium sulfate then reveals the amount of oxidant consumed. This amount is calibrated in separate experiments with known weights of the cellulose or pulp. The other half of the original alkaline liquor, containing both the beta- and the gamma-cellulose, is oxidized in the same way and the weight of the beta- fraction is obtained by difference.[70, 72] An alternative procedure is to wash, dry, and weigh the precipitated beta- fraction and to obtain the gamma-cellulose from the difference between the sample weight and the sum of the alpha- and beta-celluloses. This procedure appears to be more tedious and difficult because the physical condition of the beta-cellulose is often disadvantageous.[72] The oxidation method can also be used to estimate the alpha-cellulose after it has been dissolved in about 90 cc. of 72% sulfuric acid by weight. When this method is followed, the oxidant need not be carefully standardized in many instances, and the sample need not be accurately weighed, since the amounts of alpha-, beta-, and gamma-celluloses can be expressed as percentages of the total oxidant consumed.[70]

The variants in the alpha-cellulose determination mainly concern the manner in which the mixture of pulp and 17.5% caustic soda is diluted and washed. Since cellulose is more soluble in 8.3% than in 17.5% caustic soda, the dilution with an equal volume of water, as described above, will tend to lower the alpha-cellulose yield. Vieweg,[73] Améen and Karlsson,[74]

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[71] C. Dorée, *The Methods of Cellulose Chemistry*, pp. 246, 342; see ref. 1, p. 119.

[72] M. W. Bray and T. M. Andrews, *Ind. Eng. Chem.*, **15**, 377 (1923).

[73] W. Vieweg, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 181 (1938); *Chem. Abstracts*, **32**, 6856 (1938).

[74] W. Améen and B. Karlsson, *Svensk Papperstidn.*, **43**, 302 (1940); **43**, 314 (1940); *Chem. Abstracts*, **35**, 310 (1941).

and Steudte[68] approve of carrying out the dilution with saturated sodium chloride solution in order to counteract the tendency of the alpha-cellulose to dissolve. The yields are 1 to 3% higher by this method and correspond more closely to those obtained in the viscose process. A similar result is secured by oxidizing an aliquot of the undiluted, 17.5% caustic soda mother liquor and estimating the alpha-cellulose by difference.[75]

Solubilities are occasionally determined in alkaline conditions other than those described above. Boiling 1% solutions of caustic soda or of saturated barium hydroxide have been used in the textile field,[76] and hot 7.14% caustic soda or 10% caustic potash by nitrators of cellulose.[77] The necessity for a rigorous standardization of the experimental conditions applies with equal force in these and similar tests.

(e) *Viscosity*

The determinations of the viscosity of celluloses in cuprammonium are based for the most part on the work of Clibbens and Geake,[78] who minimized the effects of atmospheric oxidation and of variation in the composition of the solvent by suitable, rigorously standardized technique. The following brief outline of the method is based upon the detailed descriptions given by Dorée,[79] by the American Chemical Society Committee on the Viscosity of Cellulose,[80] by Mease,[81] and by Clibbens and Little.[82]

The best way of preparing the cuprammonium solution[83] is to bubble air first through strong ammonia and then up through copper turnings, or reprecipitated copper, immersed in a column of the same liquid, which is kept near 0°C. The solution of the copper is facilitated if the surface of the metal is previously cleaned with dilute hydrochloric acid and if the ammonia contains 1 to 10 g. of sucrose per liter. After some hours, when more than enough copper is considered to have passed into solution, the clear, supernatant blue liquor is analyzed by standard inorganic methods for copper, ammonia, and nitrite. If the latter exceeds 0.5%, difficulty may be experienced in dissolving high-viscosity samples. The liquor is then diluted with aqueous ammonia in such volume and of such strength as to make the final solution conform to the specifications of the particular method followed. Solutions containing 30 ± 2 g. of copper and 165 ± 2 g. of

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[75] H. Tydén, *Svensk Papperstidn.*, **43**, 221 (1940); *Chem. Abstracts*, **34**, 8259 (1940)
[76] C. Dorée, *The Methods of Cellulose Chemistry*, p. 123; see ref. 1, p. 119.
[77] D. F. J. Lynch, *Ind. Eng. Chem.*, **22**, 952 (1930).
[78] D. A. Clibbens and A. Geake, *J. Textile Inst.*, **19**, T77 (1927).
[79] C. Dorée, *The Methods of Cellulose Chemistry*, pp. 48–75; see ref. 1, p. 119.
[80] E. K. Carver and committee, *Ind. Eng. Chem., Anal. Ed.*, **1**, 49 (1929).
[81] R. T. Mease, *J. Research Natl. Bur. Standards*, **22**, 271 (1939).
[82] D. A. Clibbens and A. H. Little, *J. Textile Inst.*, **27**, T285 (1936).
[83] R. A. Joyner, *J. Chem. Soc.*, **121**, 1511 (1922).

ammonia per liter[80] are said by Conrad[84] to dissolve raw cottons much more readily than those containing 15 g. of copper and 200 g.[85] or 240 g.[81] of ammonia per liter. The latter are suitable for most technical materials and are probably more widely used. Cuprammonium solutions can be preserved for some months if kept under an inert gas near 0 °C. and in the dark.

The major difficulty connected with the solution of the sample, which may take many hours of gentle agitation at room temperature, lies in the necessity of avoiding oxidative degradation and degradation by light. Oxygen-free atmospheres of nitrogen or hydrogen are frequently prescribed, together with appropriate but rather elaborate equipment.[78–81] Solution may take place in a separate vessel and be followed by a transfer to the viscometer[86, 87, 88] or the latter itself may be charged with known amounts of sample and solvent.[89] The more recent methods avoid both oxidative degradation and the use of an inert gas by keeping the vessel containing the sample completely filled with solvent during the process of solution. In these cases, the vessel contains a glass, or stainless steel, or mercury, plunger to agitate the mixture as the vessel is slowly turned end for end on a vertical wheel. The effects of a brief exposure of the solution to air during transfer to a viscometer are inconsiderable in many cases.[86, 87] Several attempts have been made to simplify the technique to the point where cuprammonium viscosities could serve as a quick, technical control method.[90, 91] In this connection, Rich[92] has found that many freshly prepared pulps dissolve in cuprammonium in 1 min., instead of in several hours, if they are dried through the use of acetone rather than directly from water and are then soaked in strong ammonia. Most methods arrange matters so that the concentration of the solution is 0.5% for high-viscosity samples and 2% for rayons and the more highly degraded pulps. When the viscosity is known at one concentration, that at another can usually be predicted by means of the empirical relationships described in Chapter IX, E and F.

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[84] C. M. Conrad, *Ind. Eng. Chem., Anal. Ed.*, **13**, 526 (1941).

[85] Tech. Assoc. Pulp Paper Ind., *Standards*, T 206 m-35.

[86] R. T. Mease, *J. Research Natl. Bur. Standards*, **27**, 551 (1941).

[87] F. Schütz, W. Klauditz, and P. Winterfeld, *Papier-Fabr.*, **35**, Tech.-wiss. Tl., 117 (1937); *Chem. Abstracts*, **31**, 5160 (1937).

[88] H. Doering, *Papier-Fabr.*, **38**, Tech.-wiss. Tl., 80 (1940); *Chem. Abstracts*, **34**, 7602 (1940).

[89] Am. Soc. Testing Materials, *Standards*, III, D 539-39 T (1939).

[90] K. Fabel, *Kunstseide*, **18**, 5 (1936); *Chem. Abstracts*, **30**, 2365 (1936).

[91] E. Ennevaara, *Pacific Pulp & Paper Ind.*, **10**, No. 11, 20 (1936); *Chem. Abstracts*, **31**, 2422 (1937).

[92] E. D. Pich, *Paper Trade J.*, **112**, 35 (Feb. 6, 1941).

The construction, dimensions, and use of viscometers are fully explained in the references cited,[78–82, 93] and the anomalous viscosity phenomena displayed by cellulose are discussed in Chapter IX, E and F. Here, it is only necessary to remark that if a fixed volume of solution of viscosity η and density d takes t seconds to run out through the capillary of a capillary viscometer, then $\eta = d\,(At - B/t)$. The term B/t makes allowance for the kinetic energy of the emerging liquid and is inconsiderable unless the viscosity is low, when the flow is rapid and t is small. Falling-sphere viscometers are often employed with liquids of considerable viscosity and in this case the estimation consists of noting the time it takes a glass or stainless steel ball to fall through a fixed depth of the solution. The relationship is then $\eta = Kt\,(d_1 - d)$, where d_1 is the density of the ball. The constants A and B, or K, are determined separately for each viscometer by noting the times for two or more liquids whose viscosities in c.g.s. units (poises) are independently known and are in the viscosity range for which the particular instrument is designed. These liquids may be aqueous solutions containing standard concentrations of pure glycerol, or preferably of sucrose, and pure, organic substances like benzyl or phenylethyl alcohol are also used.[82] The determinations are usually made at 20 or 25°C. and it is necessary to use a viscometer designed for the range that includes the viscosity of the unknown. A few minutes spent in timing with a stop watch then gives the data from which the viscosity in poises, or centipoises, is readily calculated. High-grade cotton in 0.5% solution may have a viscosity as high as half a poise, or 50 cps. The reciprocal of the former value (for example, 2) is the *fluidity* of the solution, whose inverse linear relationship to the tensile strength of a cotton will be discussed later (see Section I, 2 of this chapter). Rayons may have fluidities as high as 40, but no tensile strength remains in a fiber when the value of 60 is reached.[82]

The trouble of preparing and standardizing cuprammonium and of protecting it and its solutions from light and oxidation has induced several investigators to study other solvents in which to determine the viscosity of cellulose. Aqueous 1.96 N dibenzyldimethylammonium hydroxide (Triton F) was used by Russell and Woodberry,[94] who stirred 0.05-g. samples of finely divided, air-dry cotton with about 10 cc. of the solvent in a test tube and poured the resulting bright, transparent solution into the viscometer. High-viscosity cotton was dissolved after 2.5 hrs. of mechanical stirring at 20 to 25°C. No precautions were necessary to protect the system from air provided the viscosity was measured within half

[93] M. R. Cannon and M. P. Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 297 (1938).

[94] W. W. Russell and N. T. Woodberry, *Ind. Eng. Chem., Anal. Ed.*, **12**, 151 (1940).

an hour after solution was complete, and the precision of the measurements was about 2%.

When the viscosity of a solution is divided by that of the solvent, measured of course under the same conditions, the quotient is called the *relative viscosity*, η_r, of the solution. Since this value indicates the number of times the presence of the solute increases the viscosity of the solvent, the quantity η_r-1 represents, at least as far as simple arithmetic is concerned, the contribution of the dissolved material. This contribution is called the *specific viscosity*.

Russell and Woodberry found that the fluidities in Triton F were about one-tenth of those in cuprammonium but that the specific viscosities were about twice as large. Much more extensive studies of fluidity and viscosity relationships were made by Brownsett and Clibbens[95] for solutions of cellulose in cuprammonium, Triton F, cupri-ethylenediamine, benzyltrimethylammonium hydroxide (Triton B), and caustic soda. The last two have only a limited solvent action on high-viscosity samples but the first three are generally available for viscosity determinations, although the numerical data will depend upon which is chosen. Mease and Gleysteen[96] compared the convenience of measuring viscosities in cuprammonium, Triton F, and by a xanthation method in which the cellulose was dissolved in a mixture of caustic soda and carbon disulfide, but made no specific recommendations. Straus and Levy,[97] however, preferred an aqueous solution of ethylenediamine which was 0.5 *M* in copper. This solvent was easy to prepare and to standardize, dissolved cotton as readily as cuprammonium, and the solution suffered no drop in viscosity during exposure to air for 3 or 4 hrs. The solution of the cellulose could therefore be carried out without special precautions or the use of an inert gas. At the present time, it accordingly seems that cupri-ethylenediamine and Triton F are the most promising alternatives to cuprammonium as a solvent for routine determinations of the viscosity of cellulose and pulps.

Another convenient procedure has been emphasized by Berl,[98] whose earlier work with Rueff[99] showed that cellulose was degraded little or not at all when nitrated with a mixture consisting of 50 to 60% nitric acid, 25 to 35% phosphoric acid, and 5 to 15% phosphorus pentoxide. After

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[95] T. Brownsett and D. A. Clibbens, *J. Textile Inst.*, **32**, T32, T57 (1941).

[96] R. T. Mease and L. F. Gleysteen, *J. Research Natl. Bur. Standards*, **27**, 543 (1941).

[97] F. L. Straus and R. M. Levy, *Paper Trade J.*, **114**, 31 (Jan. 15, 1942). This article reviews the literature.

[98] E. Berl, *Ind. Eng. Chem., Anal. Ed.*, **13**, 322 (1941).

[99] E. Berl and G. Rueff, *Cellulosechem.*, **12**, 53 (1931).

nitration for 5 min., the excess nitration liquor was removed, and the undissolved cellulose nitrate was immersed in 50% alcohol at −10 to −30°C. Stabilization by boiling for 5-min. periods in three changes of 96% alcohol and drying, first through peroxide-free ether and then at 60°C. or less, completed the process, which occupied a total of about 45 min. Viscosity determinations with 0.25% solutions of the nitrate in acetone or, preferably, in butyl acetate were then carried out at leisure, since no problem of possible oxidative degradation was involved. Davidson[100] used a mixture containing 48% of nitric acid, 50% of phosphoric acid, only 2% of phosphorus pentoxide, and used a cellulose to a nitration liquor ratio of 1 to 100. Products prepared at 0 and 20°C. had the same fluidity, and nitrations of a hydrocellulose at intervals over a period of eighteen months gave products of the same fluidity (39.4, 38.4, 39.3, 38.5, and 39.5). Davidson's nitration conditions required 2 to 4 hrs. at 0°C. to produce nitrates of maximum solubility and maximum nitrogen content (N = 13.7 to 13.9%). These nitrates contained 0.2 to 0.4% of phosphorus.

(*f*) *Degrees of Polymerization and of Polymolecularity*

Much experience with solutions of linear macromolecules convinced Staudinger that the ratio of the specific viscosity to the concentration, $\frac{\eta_{sp}}{c}$, becomes independent of the concentration when c is sufficiently small, and that this ratio is proportional to the weight-average molecular weight ($\eta_{sp}/c = K_m \mathbf{M}_w$). When c is expressed as a fraction of the base molar concentration (16.2 weight per cent), K_m for cellulose in cuprammonium[101, 102] is 5×10^{-4}. In a typical experiment,[103] a 0.0267% solution of lightly bleached linters had a relative viscosity of 1.148 and specific viscosity of 0.148. The quantity $\frac{\eta_{sp}}{c}$ was therefore $\frac{0.148 \times 16.2}{0.0267}$, or 87.5, and the molecular weight was $\frac{87.5}{5 \times 10^{-4}}$, or 175,000, resulting in an average degree of polymerization (D.P.) of $\frac{175{,}000}{162}$, or 1080. Staudinger and Daumiller[103] also tabulated the K_m constants for cellulose dissolved

[100] G. F. Davidson, *J. Textile Inst.*, **29**, T195 (1938).
[101] H. Staudinger and G. Daumiller, *Ann.*, **529**, 219 (1937).
[102] H. Staudinger and R. Mohr, *Ber.*, **70B**, 2296 (1937).
[103] H. Staudinger and G. Daumiller, *Ber.*, **70B**, 2508 (1937).

in cupri-ethylenediamine (8.0×10^{-4}), tetraethylammonium hydroxide (4.2×10^{-4}), and in other inorganic solvents.

The concentrations required for $\frac{\eta_{sp}}{c}$ to become approximately constant are of the order of 0.05 to 0.1% for high-viscosity cottons and are somewhat larger for more degraded samples. The determination of the specific viscosity of these very dilute solutions involves appreciable error since the viscosity of the solution is only slightly greater than that of the solvent. A more serious difficulty lies in the disastrous effect of even a trace of oxidative degradation in such dilute solutions, particularly when the sample is highly polymerized. The completely enclosed, oxygen-free, nitrogen-containing equipment used by Staudinger and his collaborators[104] for the preparation of the solution and the determination of the viscosity has been described by Lottermoser and Wultsch.[105] Neale and Waite[106] have also outlined their technique, in which degradation was avoided by the use of hydrogen. The actual determination of viscosity is usually made in viscometers of an all-enclosed Ostwald type. Neale and Waite[106] were unable to confirm the claim that $\frac{\eta_{sp}}{c}$ becomes constant at very low dilutions. They preferred to express c as concentration in per cent instead of as base moles, and to plot $\frac{\eta_{sp}}{c}$ against the concentration c. The $\lim \left(\frac{\eta_{sp}}{c}\right)_{c \to 0}$, called the *intrinsic viscosity* $[\eta]$, could be obtained with a probable error of 5 to 10% when the composition of the cuprammonium was known. Kraemer and Lansing's[107] relationship, D.P. $= 260\,[\eta]$, was then used to calculate the degree of polymerization. When the nitration method is used, the base molal concentration is about 28% instead of 16.2% and Staudinger's K_m constant[102] becomes 11×10^{-4}. The corresponding Kraemer and Lansing relationship is D.P. $= 270\,[\eta]$ for acetone solutions.

The determination of polymolecularity involves the fractionation of the sample according to chain length by one of the methods discussed in Section D of this chapter; followed by the determination of the average D.P. of the individual fractions, usually by one of the techniques discussed above or by the ultracentrifuge. Most of the satisfactory studies of the polymolecularity of pulps have up to now been carried out by the nitra-

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[104] H. Staudinger and A. W. Sohn, *Ber.*, **72B**, 1709 (1939), footnote 4.
[105] A. Lottermoser and F. Wultsch, *Kolloid-Z.*, **83**, 180 (1938).
[106] S. M. Neale and R. Waite, *Trans. Faraday Soc.*, **37**, 261 (1941).
[107] E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 153 (1935).

tion method. The following example happens to be taken from the work of Jurisch.[108]

The pulp, nitrated without degradation and weighing 2.5 g., was dissolved in 500 cc. of pure acetone contained in a brown flask of Jena glass, since nitrocellulose is sensitive both to light and to the alkali in ordinary glass. Traces of undissolved impurities were filtered or centrifuged away and 80 cc. of the solution was precipitated in methanol. After drying at not more than 50°C., the weight of the precipitate gave the exact concentration of cellulose nitrate in the liquid and its Staudinger viscosity gave the weight-average D.P. of the original material. A second portion, 320 cc., of the liquid was held at a closely constant temperature (about 20°C.) and steadily agitated while water was added dropwise from a buret. After about 30 cc. had been added, a slight turbidity signalized the precipitation of the first fraction. This fraction was separated on the centrifuge with care to avoid evaporation. The precipitates separated in triplicate estimations after 5 min., 6 hrs., and 24 hrs. standing in contact with the mother liquor weighed 12.0, 11.8, and 12.5 mg., respectively, and had D.P.'s of 980, 960, and 990, respectively. The fractionation was therefore not altered by the time of standing. Seven or eight fractions of decreasing D.P. were obtained as the water in the acetone solution was increased stepwise from about 10% to about 13.5%. Each fraction was dissolved in the minimum volume of acetone and precipitated from this solution by the addition of an equal bulk of methanol, followed by a little water in order to facilitate filtration. After drying at 50°C., Staudinger viscosities were determined in acetone solution.[102] The weights and the degrees of polymerization of the several fractions provided the data from which the polymolecularity of the original pulp was charted (see Section D of this chapter). Since a small amount of the original material was often lost mechanically during the manipulations, the percentage amount of each fraction was calculated from the total weight recovered and not from the weight of the original sample. The whole analysis, from pulp to polymolecularity plot, was completed within 24 hrs.

(g) *Distinctions between Hydro- and Oxy-celluloses*

The presence of these degradation products in textiles and elsewhere is reliably indicated by loss in strength, especially after treatment with alkali, by an increased affinity for many dyestuffs, and frequently, but not invariably, by the presence of an increased number of carbonyl groups. When the available sample is sufficient, it may be nitrated without further degradation[98, 99, 100] and the viscosity of the nitrate may be determined. If an alkaline treatment prior to nitration leaves the viscosity almost unchanged, the original sample was a hydrocellulose, while a substantial decrease is characteristic of an oxycellulose.[100, 104] This test, of course, is liable to fail if the sample has already undergone an alkaline treatment or if the viscosity is directly determined in cuprammonium or Triton F, because the alkalinity of such solvents is quite sufficient to degrade some oxycelluloses during the process of solution.[95, 104] Acidic groups, which are

[108] I. Jurisch, *Chem.-Ztg.*, **64**, 269 (1940).

absent in hydrocelluloses unless traces of inorganic or organic esters are present,[109] can be detected in oxycelluloses by the fixation of dyestuffs like methylene blue, by titrimetric methods, and usually by the liberation of "uronic acid" carbon dioxide (see p. 147).

When only a minute sample, untreated with alkali, is available, recourse must be had to numerous qualitative tests toward which oxycelluloses usually react much more strongly than hydrocelluloses. Ditz[110] and Ditz and Ullrich[111] employed a modification of Nessler's reagent made by dissolving 8 g. of potassium iodide and 10 g. of red mercuric iodide in 50 cc. of water and diluting the solution with 500 cc. of 3 *N* caustic soda. The solution was filtered through glass wool the next day. This reagent stained various oxycelluloses either yellow, orange, brown, or gray, depending upon the extent of the reduction to mercurous salt and free mercury, and the depth of color increased for 24 hrs. Hydrocelluloses were stained only yellow or orange under the same circumstances. The differential staining of reducing oxycelluloses by the precipitation of either Prussian or Turnbull's blue has been known since the time of Cross and Bevan, and modifications have been suggested by Ermen[112] and Thomas.[113] The former used stock solutions, the first of which contained 20 g. of ferric sulfate and 25 g. of ammonium sulfate in 100 cc., and the second had 33 g. of potassium ferricyanide in the same volume. Five cc. of each solution was added to 250 cc. of distilled water, the mixture was brought to the boil, and the sample was immersed for 1 min. The dyed sample was rinsed in dilute sulfuric acid and water. Müller,[114] working with a similar solution, confirmed the claim that oxycelluloses stained deep blue and that cotton was slightly stained. Hydrocellulose became a bright blue-green.

It will be seen that the above tests, together with the absorption of dyestuffs like methylene blue and the copper reduction test, make no general, clean-cut distinction between oxy- and hydro-celluloses. Müller,[114] who stripped dyestuffs from the original material by immersion for 10 min. in 0.2% sodium hyposulfite at 80 to 90°C., noted that this treatment very greatly increased the response of oxycelluloses but not hydrocelluloses to the above tests. He adopted the hypothesis that the reactivity of the aldehyde groups in hydrocelluloses is depressed by hemiacetal formation to the point where they react more sluggishly than some of the exposed carbonyls in reducing oxycelluloses. He supposed that hyposulfite did not add to the hydrocellulose but that its ready addition to oxycelluloses greatly enhanced their reducing power and affinity for dyestuffs. The

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[109] Methods for the detection and estimation of traces of mineral acids are given by C. Dorée, *The Methods of Cellulose Chemistry*, pp. 181–9; see ref. 1, p. 119.

[110] H. Ditz, *J. prakt. Chem.*, **78**, 343 (1908).

[111] H. Ditz and F. Ullrich, *J. prakt. Chem.*, **147**, 167 (1936).

[112] W. F. A. Ermen, *J. Soc. Dyers Colourists*, **44**, 303 (1928); **51**, 127 (1935).

[113] H. A. Thomas, *J. Soc. Chem. Ind.*, **52**, 79T (1933).

[114] F. Müller, *Helv. Chim. Acta*, **22**, 208, 217 (1939).

ame line of thought led him to examine the typical carbonyl reagents, nd substituted α-naphthyl-, diphenyl-, and other complicated aromatic ydrazines were claimed to condense only with the carbonyl groups of xycelluloses. The sulfonic acid or sodium sulfonate derivatives were sed in approximately 1% aqueous solution and after 1 hr. at the boiling oint the sample was removed and washed. The presence of the sulfonic roups caused a greatly increased absorption of methylene blue. It was lso possible to couple the hydrazides with suitable diazo derivatives and orm dyestuffs. 2-Diphenyldihydrazinedisulfonic acid, 1-hydrazinonaphhalene-3,6.8-trisulfonic acid and the stabilized diazo compounds *Echtblausalz B* and *Variaminblausalz FG* are examples of the derivatives used. The coupling of the diazo salts was carried out in faintly alkaline solution of about 0.05% concentration and after 10 to 15 min. the reagent was washed away and the dyed fibers were treated with a hot soap solution.

When the sample has been exposed to alkali prior to examination, undegraded cotton and hydrocellulose may be swollen and may become mercerized to some extent, but oxycellulose also suffers the loss of most, or practically all, of its carbonyl groups. Tests which depend upon distinctions in colloidal surface or reducing properties therefore tend to fail, and a differentiation between hydro- and oxy-celluloses frequently becomes a very difficult matter, particularly with microscale samples. Haller accordingly based his tests upon the fact that even after alkaline treatment oxycelluloses still possess many acidic groups. The fibers were soaked in 1% stannous chloride solution for 3 to 4 hrs.,[115] whereupon the acidic groups apparently absorbed stannous tin. Subsequent washing with water and immersion in a dilute solution of tetrachloroauric acid, which must be distinctly yellow in color, produced the well-known Cassius gold purple, the appearance of which differentiated alkaline-treated oxycelluloses from hydrocelluloses. A similar Haller test[116] employed a 1% lead acetate solution for 30 min., followed by careful washing at 80°C., and the development of a violet color with a 0.05% paste of cochineal at 50°C.[117]

Many other tests of varying value are tabulated in Herzog and Koch's[118] comprehensive review of the literature. The sensitivity of the various

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[115] R. Haller, *Helv. Chim. Acta*, **14**, 578 (1931); *Melliand Textilber.*, **12**, 257, 517 (1931). These articles review other tests.

[116] R. Haller and F. Lorenz, *Melliand Textilber.*, **14**, 449 (1933).

[117] *Gmelin-Kraut's Handbuch der anorganischen Chemie*. Vol. 4, part 2, Carl Winter's Universitätsbuchbehandlung, Heidelberg, 1924, p. 840.

[118] A. Herzog and P. A. Koch, *Melliand Textilber.*, **18**, 785 (1937).

tests was also discussed by Forster, Kaji, and Venkataraman,[119] who distinguished between oxy- and hydro-celluloses by means of rubeanic acid.

3. Additional Estimations Required for High-Polymer Impurities[120]

(*a*) *Lignin*

Modern estimations consist of hydrolyzing the carbohydrate portion of the sample with strong mineral acid and in isolating, drying, and weighing the dark, undissolved residue, which is accepted as lignin. Cold, 42% hydrochloric acid[121–123] is often used, particularly with cereal grasses,[124, 125] but sulfuric acid is more customary for woods and pulps.[126] Since part of the breakdown products from any fats, waxes, resins, tannins, and proteins may become insoluble during the acid treatment of the sample, the apparent lignin may be high unless these interfering substances are removed by a previous extraction with suitable solvents.[127, 128, 129] On the other hand, these extractions may dissolve some lignin and render the result low.[130, 131] Similar considerations apply to the alkaline pretreatments designed to remove sensitive, interfering carbohydrates that might give insoluble, humic acid products in the presence of mineral acids.[130–137]

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[119] R. B. Forster, S. M. Kaji, and K. Venkataraman, *J. Indian Chem. Soc., Industrial Ed.*, **1**, 36 (1938); *Brit. Chem. Abstracts*, **B1938**, 1024.

[120] C. Dorée, *The Methods of Cellulose Chemistry*, pp. 446–54 (see ref. 1, p. 119), gives more detailed descriptions of many tests.

[121] R. Willstätter and L. Zechmeister, *Ber.*, **46**, 2401 (1913).

[122] E. Hägglund and C. J. Malm, *Cellulosechem.*, **4**, 73 (1923); *Chem. Abstracts*, **18**, 327 (1924).

[123] H. Urban, *Cellulosechem.*, **7**, 73 (1926); *Chem. Abstracts*, **20**, 3080 (1926).

[124] M. J. Goss and M. Phillips, *J. Assoc. Official Agr. Chem.*, **19**, 341 (1936).

[125] M. Phillips and M. J. Goss, *J. Assoc. Official Agr. Chem.*, **19**, 350 (1936).

[126] P. Klason, *Cellulosechem.*, **4**, 81 (1923); *Chem. Abstracts*, **17**, 3788 (1923); **18**, 327 (1924).

[127] G. J. Ritter and J. H. Barbour, *Ind. Eng. Chem., Anal. Ed.*, **7**, 238 (1935).

[128] J. G. Shrikhande, *Biochem. J.*, **34**, 783 (1940).

[129] M. Phillips, *J. Assoc. Official Agr. Chem.*, **22**, 422 (1939).

[130] E. E. Harris and R. L. Mitchell, *Ind. Eng. Chem., Anal. Ed.*, **11**, 153 (1939).

[131] I. A. Preece, *Biochem. J.*, **35**, 659 (1941).

[132] E. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **5**, 105 (1933).

[133] K. F. Bamford and W. G. Campbell, *Biochem. J.*, **34**, 419 (1940).

[134] K. Freudenberg and T. Ploetz, *Ber.*, **73B**, 754 (1940); *Cellulosechem.*, **18**, 49 (1940).

[135] T. Ploetz, *Cellulosechem.*, **18**, 57 (1940).

[136] M. Phillips and M. J. Goss, *J. Assoc. Official Agr. Chem.*, **21**, 141 (1938).

[137] A. G. Norman, *The Biochemistry of Cellulose, Polyuronides, Lignin, Etc.*, Clarendon Press, Oxford, 1937, pp. 167–77, discussed possible interferences in the lignin estimation.

Chemical pulping processes eliminate the greater part of the interfering substances together with all but a few per cent of the lignin, and the determination of the residual amount of the latter need not as a rule be preceded by extractions. It is, however, essential that the acid treatment be drastic enough to dissolve all carbohydrates and at the same time be mild enough to avoid the formation of carbonaceous substances. In other words, the apparent lignin value must be a minimum one and the requisite conditions may vary somewhat with different woods and pulps. The following outline is based on the work of Ritter, Seborg, and Mitchell.[138]

Approximately 2 g. of the finely divided, air-dry pulp of known moisture content is thoroughly mixed, at 20 °C., with 25 cc.,[138] or 40 cc., of 72 ± 0.1% sulfuric acid by weight in such a way that the rise in temperature is inconsiderable. After 2 hrs., or longer, when the mixture appears as dark flecks suspended in a water-clear, not very viscous solution, the acidity is reduced to 3% by dilution with distilled water, and the hydrolysis of the carbohydrates is completed by boiling under a reflux condenser for 3 hrs. The lignin residue is isolated, thoroughly washed with hot water, and dried in an air oven at 105 °C. to constant weight, which may be corrected when desirable for a small ash content or for a trace of combined or absorbed sulfuric acid.[134] Bailey,[139] and also Stumpf and Wiesenberger,[140] adapted the method to a microscale (3- to 10-mg. samples) and similar work by Wiechert[141] employed liquid hydrogen fluoride to dissolve the carbohydrate in a 200-mg. sample. The latter method in some cases gave slightly lower lignin values than the standard macro procedures.

The pulping industry has been interested for years in rapid lignin estimations, suitable for plant control, because the lignin content of pulps has a marked effect upon their physical properties and upon the amount of oxidant required for bleaching.

Roe's[142] *chlorine number* is defined to be the number of grams of the gas that is absorbed in 15 min., at 20 °C., by 100 g. of oven-dry pulp after moistening with 125 g. of water. About 2 g. of the dry pulp is transferred to a weighed vessel and steam, or water, is added until the increase in weight is 2.5 g. A system of the type used in gas analysis[143] is employed to expose the moistened sample to an atmosphere of chlorine at ordinary pressure and to maintain the temperature near 20 °C. during the exothermic reaction. The volume of chlorine absorbed in 15 min. is corrected for a small blank caused by the

[138] G. J. Ritter, R. M. Seborg, and R. L. Mitchell, *Ind. Eng. Chem., Anal. Ed.*, **4**, 202 (1932).

[139] A. J. Bailey, *Mikrochemie*, **19**, 98 (1935).

[140] W. Stumpf and E. Wiesenberger, *Cellulosechem.*, **18**, 103 (1940); *Chem. Abstracts*, **35**, 6442 (1941).

[141] K. Wiechert, *Cellulosechem.*, **18**, 57 (1940); *Chem. Abstracts*, **35**, 6442 (1941).

[142] R. B. Roe, *Ind. Eng. Chem.*, **16**, 808 (1924). This article gives literature references. See also Tech. Assoc. Pulp Paper Ind., *Standards*, T 202 m-40.

[143] G. P. Genberg and E. O. Houghton, *Paper Trade J.*, **88**, 71 (Apr. 25, 1929), gave a detailed description of the method.

solubility of the gas in the 2.5 g. of water. Similar estimations depend upon bromination[142] and upon chlorination with standard calcium hypochlorite solutions.[144] Another quick estimate of the lignin content of pulps can be obtained from the *permanganate number*,[145] which was defined by Wiles[146] as the number of cc. of 0.1 *N* potassium permanganate reduced by 1 g. of oven-dry sample when the conditions are strictly standardized. The air-dry sample, of known moisture content, is thoroughly disintegrated in a known volume of distilled water and the mixture is made 0.03 *N* in permanganate and 0.133 *N* in sulfuric acid by the addition of suitable amounts of the 0.1 *N* and the 4 *N* solutions, respectively. A pilot determination is often run to make sure that an excess of the oxidant is used. After 5 min. at 25°C., the oxidation is stopped by adding 5 cc. of *N* potassium iodide. and the liberated iodine, corresponding to the unused excess of permanganate, is titrated with standard sodium thiosulfate solution.[147] An alternative procedure is to stop the oxidation with an excess of standard ferrous ammonium sulfate and to carry out a back titration with standard potassium dichromate. The exact relationship of the chlorine and permanganate numbers to the lignin content of pulps still seems to be in doubt, although in certain circumstances the three estimations increase together in a linear, or nearly linear, fashion.[148]

One of the characteristics of lignin, or perhaps of substances closely associated with it, is that it is stained yellow or red with solutions containing one of the large number of phenols and primary and secondary amines tabulated by Fuchs.[149] Qualitative or semiquantitative methods of estimation can be based upon the intensity of color in standard conditions or upon the amount of phenol or amine withdrawn by the lignin from solution. A 0.5% solution of phloroglucinol in 10% hydrochloric acid was used by Cross, Bevan, and Briggs[150] and the unabsorbed excess was titrated with a standard solution of furfural or formaldehyde with the lignin in newspaper as an indicator. Dunnicliff and Suri[151] later improved the technique. The test with aniline acetate is well known and Schickh[152] has suggested that the red stain developed by lignin-containing pulps in the presence of 2,6-diaminopyridine and 18 to 36% hydrochloric acid might also be of value. A rather different colorimetric method was published by Mehta[153]

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[144] C. M. Koon, *Paper Trade J.*, **111**, 34 (Aug. 8, 1940); *Tech. Assoc. Papers*, Ser. **23**, 222 (1940).

[145] B. Johnsen and J. L. Parsons, *Pulp Paper Mag. Can.*, **21**, 53 (1923); *Chem. Abstracts*, **17**, 876 (1923).

[146] R. H. Wiles, *Paper Trade J.*, **98**, 34 (Mar. 15, 1934).

[147] Tech. Assoc. Pulp Paper Ind., *Standards*, T 214 m-37.

[148] R. R. Fuller, *Tech. Assoc. Papers*, Ser. **23**, 463 (1940).

[149] W. Fuchs, *Die Chemie des Lignins*. J. Springer, Berlin, 1926, pp. 6–17. Phenols may also give green and blue colors with lignin.

[150] C. F. Cross, E. J. Bevan, and J. F. Briggs, *Ber.*, **40**, 3119 (1907).

[151] H. B. Dunnicliff and H. D. Suri, *Analyst*, **57**, 354 (1932).

[152] O. von Schickh, *Angew. Chem.*, **49**, 362 (1936).

[153] M. M. Mehta, *Biochem. J.*, **19**, 958 (1925).

or alkaline solutions of lignin. Such solutions become deep blue when oiled with Folin and Denis' phosphotungstomolybdic acid reagent[154] and he depth of color was compared with that observed in control solutions containing known amounts of lignin. Other color reactions depending on the henolic nature of lignin include the change to yellow-brown when lignin-ontaining samples are chlorinated and the subsequent change to pink or nagenta upon treatment with very slightly alkaline, aqueous sodium sulfite, s in the Cross and Bevan pulping process.[155]

It is important to make sure that lignin is absent from a pulp before etermining the percentages of alpha-, beta-, and gamma-cellulose because ny lignin present will distribute itself between the three fractions and ender the result inaccurate. The data, of course, can be corrected by neans of separate lignin estimations on the three fractions. When used vith judgment and in conjunction with microscopic observations, a knowledge of the lignin content enables the percentages of mechanical and hemical pulp to be assessed in a mixture of the two, provided that the alues for the constituents are known. Genberg and Houghton,[143] for xample, found that the high lignin content of spruce groundwood corresponded to a chlorine number of 35; unbleached chemical pulp had 3, and hat of the bleached product was still less.

(*b*) *Pentosans*

Dorée[156] and Browne and Zerban[157] reviewed the large volume of research n the pentosan estimation and described the practical details of several nethods, all of which depend upon the formation of furfural when pentose ugars, or pentosans, are boiled with dilute mineral acid. The procedure till in most common use is outlined below and is the one adopted by the Association of Official Government Chemists.[158]

A 1- to 2-g. sample is distilled with 100 cc. of 12% hydrochloric acid in such a way that he distillate increases at the approximate rate of 30 cc. in 10 min. Fresh 12% acid is dded to the still in the same increments in order to maintain the original volume of quid. The operation is stopped when 360 cc. of distillate has collected and, after filtra-

[154] O. Folin and W. Denis, *J. Biol. Chem.*, **12**, 239 (1912).
[155] W. G. Campbell and J. C. McGowan, *Nature*, **143**, 1022 (1939), and earlier articles.
[156] C. Dorée, *The Methods of Cellulose Chemistry*, pp. 354–70; see ref. 1, p. 119.
[157] C. A. Browne and F. W. Zerban, *Physical and Chemical Methods of Sugar Analysis*. ohn Wiley, New York, 1941, pp. 904–24.
[158] Association of Official Government Chemists, *Official and Tentative Methods of nalysis*. 5th ed., Collegiate Press, Menasha, Wis., 1940, p. 361.

tion, the entire volume is mixed with 40 cc. of 12% hydrochloric acid containing abou 0.3 g. of pure phloroglucinol. Next morning, the dark precipitate of furfural phloroglu cide is filtered, dried at 105°C., and weighed. Reference to Kröber's Tables, which ar empirical,[156, 157] gives the corresponding weight of xylan, araban, or other pentosan i the sample.

Kullgren and Tydén[159] advocated the use of 13.15% hydrochloric aci containing 20 g. of sodium chloride because this solution had the advantag of keeping the acid concentration unchanged during the standard distil lation. Others[160] found that the Kullgren and Tydén suggestion improve the reproducibility of the data. Several attempts have been made t eliminate decomposition during the distillation and thereby render th recovery of furfural not only reproducible but quantitative. Hughes an Acree,[161] following up earlier work by others, confirmed the suggestion tha a carefully controlled steam distillation, in place of an ordinary distillation gave theoretical yields of furfural from several pentoses, although the rat of formation varied from sugar to sugar. An interesting micro method wa elaborated by Reeves and Munro,[162] who refluxed samples equivalent t 0.4 to 1.0 mg. of pentosan in 3 to 10 cc. of 12 to 15% hydrochloric acid fo 1 to 4 hrs., according to conditions. An upper layer of xylene continually removed the furfural from contact with the acid and the amount taken u in the hydrocarbon layer was estimated colorimetrically by means o aniline acetate. The results were quantitative for xylose but not for th other pentoses tried. Jayme and Sarten[163] made use of the fact that n acid is present in the vapor phase when 20 to 30% hydrobromic acid i distilled and obtained theoretical recoveries of furfural from xylose an arabinose with this acid.

Many attempts have been made to find a substitute for the phloro glucinol method of estimating furfural, for the phloroglucide is appreciably soluble and its formation, although reproducible, is not quantitative. A satisfactory alternative procedure is to add an excess of thiobarbituric aci to the dilute, acidic furfural distillate and to wash, dry, and weigh th highly insoluble furfurylidenemalonylthiocarbamide[160, 163, 164] which is pre

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[159] C. Kullgren and H. Tydén, *Ing. Vetenskaps Akad., Handl.*, **1929**, No. 94, 3; *Chem Abstracts*, **24**, 1316 (1930).

[160] C. R. Marshall and F. W. Norris, *Biochem. J.*, **31**, 1289 (1937).

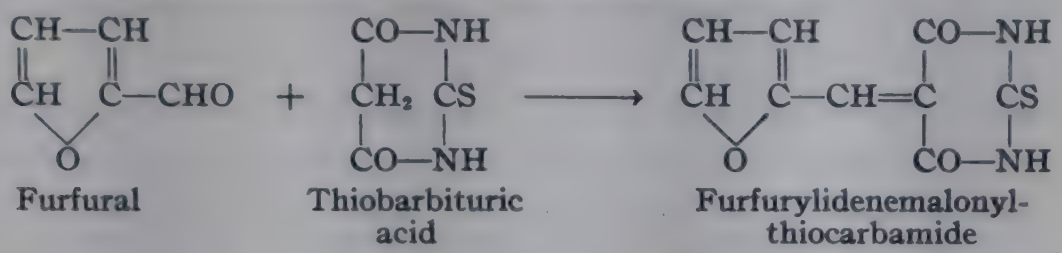
[161] E. E. Hughes and S. F. Acree, *J. Research Natl. Bur. Standards*, **23**, 293 (1939) and earlier articles.

[162] R. E. Reeves and J. Munro, *Ind. Eng. Chem., Anal. Ed.*, **12**, 551 (1940).

[163] G. Jayme and P. Sarten, *Naturwissenschaften*, **52**, 822 (1940).

[164] A. W. Dox and G. P. Plaisance, *J. Am. Chem. Soc.*, **38**, 2156 (1916).

cipitated. Although the reaction has the advantage of being stoichiometric, he precipitate is sometimes difficult to wash and filter.[165]



Another method, which is much more rapid than the precipitation procedures, is to titrate the furfural with bromine.[166, 167] Hughes and Acree[168] added 0.1 *N* potassium bromate containing 50 g. of potassium bromide per liter to the acidified distillate and titrated the excess bromine liberated from the bromate-bromide mixture with potassium iodide and standard sodium thiosulfate solution. When the reaction between the furfural and the bromine was restricted to 5 min. at 0°C., exactly one mole of the halogen was combined instead of the two or more moles taken up in a longer time or at room temperature.

Although several methods estimate furfural satisfactorily, most of them also respond to the 5-(hydroxymethyl)furfural produced in the distillate from hexoses, and to the 5-methylfurfural which is similarly derived from any rhamnose or other methylpentose units. Since the phloroglucides of hydroxymethyl- and methyl-furfural are much more soluble in alcohol than the derivative from furfural, Ellett and Tollens[169] used standardized extractions with this solvent to separate the two former from the latter. This procedure has been reported almost unanimously as inaccurate and unsatisfactory by later workers.[170] (Hydroxymethyl)furfural was observed to be much more readily decomposed than furfural by hot acid[159] and the claim was made that the redistillation of the distillate completely destroyed the former and only about 3% of the latter. This claim may not always be valid.[171] The colorimetric method with aniline acetate can also be used to estimate furfural and methylfurfural in the presence of the hydroxymethyl derivative because the latter produces a slight yellow, instead of a deep red, coloration with the reagent.[162] Since the production of (hydroxy-

[165] W. G. Campbell and L. H. Smith, *Biochem. J.*, **31**, 535 (1937).

[166] N. C. Pervier and R. A. Gortner, *Ind. Eng. Chem.*, **15**, 1167, 1255 (1923). These articles contain a bibliography of the earlier literature.

[167] W. J. Powell and H. Whittaker, *J. Soc. Chem. Ind.*, **43**, 35T (1924).

[168] E. E. Hughes and S. F. Acree, *Ind. Eng. Chem., Anal. Ed.*, **6**, 123 (1934).

[169] W. B. Ellett and B. Tollens, *Ber.*, **38**, 492 (1905).

[170] S. Angell, F. W. Norris, and C. E. Resch, *Biochem. J.*, **30**, 2146 (1936).

[171] H. F. Launer and W. K. Wilson, *J. Research Natl. Bur. Standards*, **22**, 471 (1939).

methyl)furfural in the standard distillation of pulps and papers does no exceed 0.9%,[171] the solution is usually a very dilute one which fails to giv a precipitate with thiobarbituric acid. The latter discriminates in thi case between furfural and its hydroxymethyl derivative.

A reliable differentiation between furfural and methylfurfural has als been difficult to find. Hughes and Acree[172] noted that the addition of second mole of bromine to methylfurfural at 0°C. in *N* hydrochloric aci proceeded more rapidly than in the case of furfural. A knowledge of th absolute rates, plus estimations made at different time intervals upon mixture of the two substances, obviously made it possible to calculate th composition of the mixture by substituting the data in a simultaneou equation. In one type of distillation, however, a methylpentose (rham nose) produced some acetone which took part in the final bromine estima tion and rendered the apparent yield of methylfurfural too high.[160] Mar shall and Norris[160] therefore preferred the phloroglucinol or the thiobar bituric acid estimation when dealing with methylpentoses. Quite a nove approach to the estimation of the latter in carbohydrate hydrolyzates wa made by Nicolet and Shinn,[173] who oxidized 5- to 15-mg. samples with a least a twofold excess of potassium periodate in a solution buffered t *p*H 7 to 7.2 with sodium carbonate-bicarbonate. A large excess of the amin acid, alanine (200 mg.) was present to trap the formaldehyde produced in th oxidation, but aeration with carbon dioxide gas quantitatively removed th acetaldehyde simultaneously derived from the $CH_3CHOHCHOH—$ grou of the methylpentose. This aldehyde was absorbed in sodium bisulfit solution, excess of which was afterward oxidized by iodine before the acet aldehyde-bisulfite complex was decomposed by sodium bicarbonate an estimated by titration with standard iodine. The results with rhamnos and *L*-fucitol, either separately or in admixture with glucose, xylose, o galacturonic acid, were practically quantitative and nourish the hop that the determination of methylpentosans has at last been put on a really satisfactory practical basis.

The determination of pentosans in presence of polyuronides is com plicated by the fact that the latter give 18%[174] to 25.6%[163] by weight o furfural in the pentosan estimation, the exact figure depending on th particular polyuronide and on the conditions of the acid distillation. A that can be done is to estimate the uronic acid, independently and quanti

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[172] E. E. Hughes and S. F. Acree, *Ind. Eng. Chem., Anal. Ed.*, 9, 318 (1937).

[173] B. H. Nicolet and L. A. Shinn, *J. Am. Chem. Soc.*, 63, 1456 (1941).

[174] A. G. Norman, *The Biochemistry of Cellulose, Polyuronides, Lignin, Etc.*, pp. 214 15; see ref. 137, p. 140.

tatively, by the carbon dioxide method (see below) and to subtract an appropriate amount of furfural from the total found in the pentosan determination. This procedure makes the rather doubtful assumption that the over-all yield of furfural is the exact sum of those derived from the several components of a mixture. Norris and his collaborators,[170, 175] who discussed this question, gave empirical equations connecting the uronic acid-carbon dioxide and the furfural yields with the composition of synthetic mixtures containing pentose, methylpentose, hexose, and uronic acid components. These valuable equations, like Kröber's Tables, are probably strictly valid only for the ranges and the experimental conditions actually used by the authors.

The reader is reminded that some oxycelluloses produce furfural when submitted to the standard pentosan estimation.

(c) *Uronic Acid*

Mono- and poly-saccharides in which the primary alcoholic groups of hexose units are replaced by carboxyl groups (uronic acids) lose one molecule of carbon dioxide for each acidic group when boiled with hydrochloric acid, as in the pentosan determination. Tollens and his collaborators estimated uronic acid by measuring the amount of carbon dioxide evolved in the acid treatment, either by absorbing the dried gas in weighed bulbs containing 40% caustic potash[176] or by passing the gas into excess aqueous barium hydroxide and weighing the precipitated barium carbonate.[177] Subsequent work has adhered to the principle but has improved the technique of these estimations. The following outline is based upon the work of Whistler, Martin, and Harris.[178]

The sample was heated in 12 ± 0.02% hydrochloric acid while contained in a 500-cc. flask fitted with a vertical, water-cooled reflux condenser and kept at 130 ± 0.2°C. A slow stream of carbon dioxide-free nitrogen played over the surface of the liquid. This nitrogen stream helped to carry the carbon dioxide up the condenser and through a trap containing concentrated sulfuric acid, which removed furfural and other volatile products, and over anhydrous copper sulfate, which absorbed water, traces of hydrogen chloride, and any hydrogen sulfide. The final drying was by passage through phosphorus pentoxide and the carbon dioxide was absorbed and weighed in an Ascarite tube of the type used in combustions. Other methods absorb the carbon dioxide in excess 0.1 *N*[179]

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[175] C. R. Marshall and F. W. Norris, *Biochem. J.*, **31**, 1939 (1937).

[176] K. U. Lefèvre and B. Tollens, *Ber.*, **40**, 4513 (1907).

[177] F. Mann and B. Tollens, *Ann.*, **290**, 155 (1896).

[178] R. L. Whistler, A. R. Martin, and M. Harris, *J. Research Natl. Bur. Standards*, **24**, 13 (1940). This article contains a complete literature review.

[179] D R. Nanji, F. J. Paton, and A. R. Ling, *J. Soc. Chem. Ind.*, **44**, 253T (1925).

or 0.2 N[180] barium hydroxide and back-titrate the excess with standard acid. Solution of pyridine in hydrochloric acid and of silver sulfate in sulfuric acid have been used t purify the carbon dioxide before its absorption. Buston[181] adapted the procedure t microscale samples and a semimicro method was worked out by Voss and Pfirschke.[1] The latter heated the specimen in 100 cc. of water containing 270 g. of pure zin chloride and measured the carbon dioxide volumetrically. The volumetric part of thi procedure was afterward found to give rather divergent results with pectins.[183]

It has been known for some time that cellulose and similar carbohydrate give small yields of carbon dioxide (less than 1%) in the uronic acid esti mation.[180, 184, 185] The evolution of the gas from uronic acids, however proceeds much more rapidly than from other polysaccharides,[186] and th precise rate studies of Harris and his collaborators[178] make it easy to dis tinguish between the two cases. The latter found that 207.5 mg. of carbon dioxide per g. of galacturonic acid was evolved in 3 to 5 hrs. in their equip ment and that the rate was the same for hydrochloric acid concentrations between 11 and 13%. The rate of evolution from glucose increased noticeably with the acid concentration and amounted to 2 mg. of carbon dioxide per g. after 4 hrs. heating in 12% acid. Control experiments with depectinized cellulose or with glucose therefore made it possible to estimate the true uronic acid carbon dioxide reliably, even when the absolute amount was small. Some oxycelluloses also evolve carbon dioxide when submitted to the estimation but the writer is not aware of any method for correcting the data for their presence.

(*d*) *Mannan*

The estimation of mannan has not been radically changed since the times of Bertrand[187] and of Schorger,[188] who boiled 10- to 15-g. samples of finely divided wood, or 35 to 40 g. of wet pulp,[189] under reflux with 150 cc. of 5% hydrochloric acid. This treatment hydrolyzed mannan to mannose, which was precipitated from the reconcentrated, filtered, neutralized liquors as the sparingly soluble, crystalline phenylhydrazone. Hydrolysis with

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[180] A. D. Dickson, H. Otterson, and K. P. Link, *J. Am. Chem. Soc.*, **52**, 778 (1930).
[181] H. W. Buston, *Analyst*, **57**, 220 (1932).
[182] W. Voss and J. Pfirschke, *Ber.*, **70B**, 631 (1937).
[183] K. Freudenberg, H. F. Gudjons, and G. Dumpert, *Ber.*, **74B**, 245 (1941).
[184] W. G. Campbell, E. L. Hirst, and G. T. Young, *Nature*, **142**, 912 (1938).
[185] W. V. Bartholomew and A. G. Norman, *Iowa State Coll. J. Science*, **15**, 253 (1941).
[186] A. G. Norman, *Nature*, **143**, 284 (1939).
[187] G. Bertrand, *Compt. rend.*, **129**, 1025 (1899).
[188] A. W. Schorger, *Ind. Eng. Chem.*, **9**, 748 (1917).
[189] A. Nowotnowna, *Biochem. J.*, **30**, 2177 (1936).

% sulfuric acid, followed by neutralization with barium carbonate, caused ome loss of mannose[189] and the use of 72% sulfuric acid or 40% hydro-hloric acid for 3 days at 20°C. was said to involve the destruction of practi-ally all of the sugar.[190] The loss was only about 10% in 20 hrs. at −10°C. These data seem to require confirmation because mannose is customarily solated from ivory nuts in good yield after an hydrolysis with strong sul-uric acid, which has also been recommended for the hydrolysis of mannan n pulps.[191] Although Schorger's conditions were adequate for the hydroly-is of the mannan extracted with the beta- and gamma-cellulose fractions of wood pulp,[192] Nishida, Hamashima, and Fukai[193] considered them too nild for the mannans of many woods and got better results by hydrolyzing or 45 hrs. with 5% sulfuric acid on a steam bath.

The precipitation of mannose phenylhydrazone is reported to be more atisfactory than that of the *p*-bromophenylhydrazone.[193] Even the ormer method, however, recovers mannose from admixture with other ugars in an approximately quantitative way only when the concentration exceeds 0.5%.[189, 191] This limitation necessitates the use of large pulp samples and a drastic concentration of the hydrolyzate or, alternatively, he addition of extra, weighed amounts of mannose,[190] before attempting he precipitation. The opinions concerning the time necessary for mannose henylhydrazone to crystallize completely from solution are as follows: 1 hr.,[187] 2 hrs.,[188] 24 hrs.,[192] 2 days for conifer samples, and 3 weeks for hardwoods.[193] Perhaps the best compromise is that of Nowotnowna,[189] who allowed the precipitation to proceed for 6 hrs. with constant shaking, after which the phenylhydrazone was recovered by filtration, washed in a ittle cold water, dried, and weighed.

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[190] H. Koch, *Papier-Fabr.*, **39**, Tech.-wiss. Tl., 46 (1941); *Chem. Abstracts*, **35**, 4590 (1941).

[191] E. Hägglund and L. C. Bratt, *Papier-Fabr.*, **34**, Tech.-wiss. Tl., 100 (1936); *Chem. Abstracts*, **30**, 7333 (1936).

[192] F. Lenze, B. Pleus, and J. Müller, *J. prakt. Chem.*, **101**, 213 (1920).

[193] K. Nishida, H. Hamashima, and T. Fukai, *Cellulose Ind.*, (Tokyo), **11**, 330 (1935); *Chem. Abstracts*, **30**, 3226 (1936).

I. DEGRADATION OF CELLULOSE

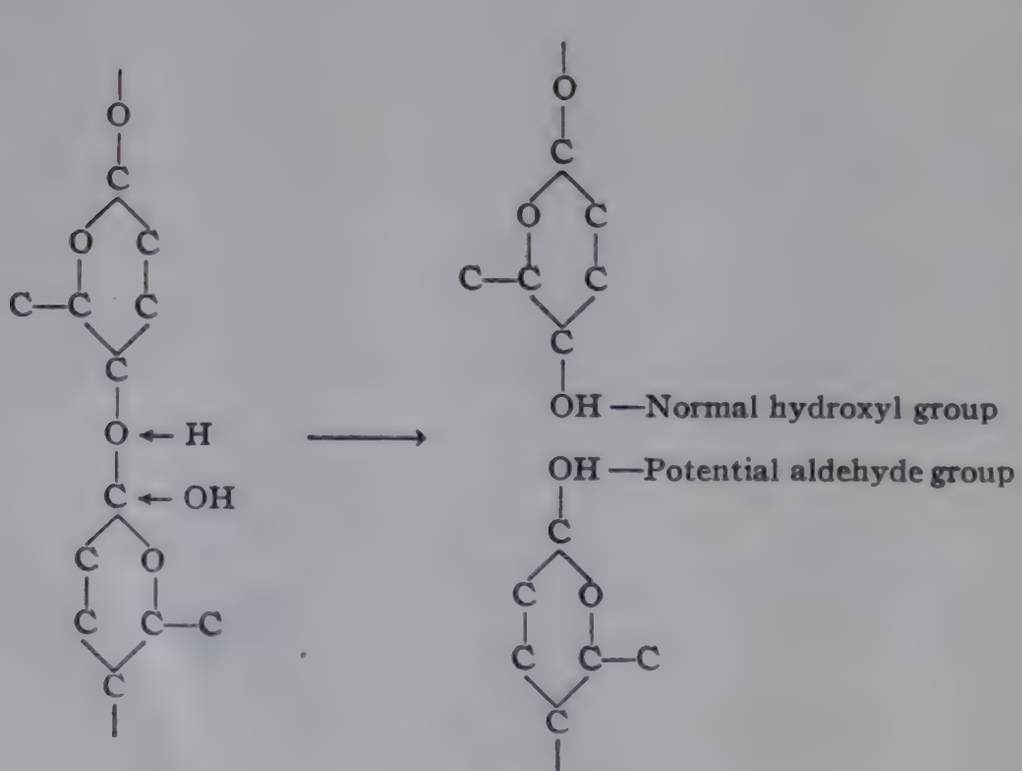
1. Kinetics of Degradation Reactions

H. MARK AND MILTON HARRIS

(*a*) *Types of Degradation Reactions*

Cellulose may be degraded chemically in several different ways but, fo the purposes of the present discussion, only degradations involving de creases in the average molecular chain length will be considered. Such degradations may result, of course, in altering the structure of the glucose residues at the ends of the chains; thus, the end residues may be oxidized hydrated, or structurally changed in a variety of ways. Nevertheless, as long as the number of new chain ends remains small, the material is still considered to be cellulose.

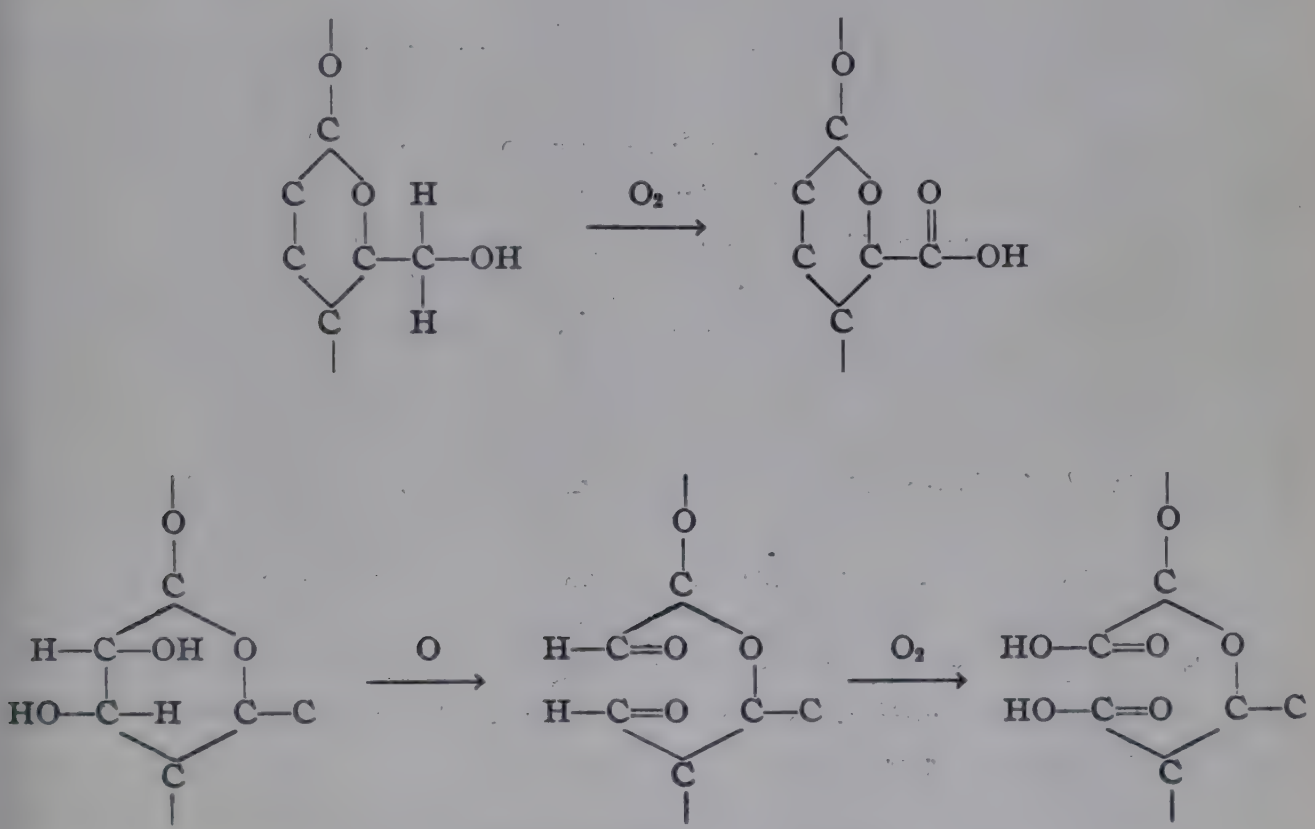
Hydrolysis. The type of degradation of cellulose which is best under- stood is that produced by the hydrolysis of the β-glucosidic bonds by the addition of water. This reaction occurs under the catalytic action of



hydrogen ions,[1–6] and can be described by the scheme on the previous page.

It leads to a product of lower average chain length and unchanged configuration of the terminal glucose residues. One of the newly formed chain ends in the above scheme represents a potential aldehyde group, and hence exhibits reducing power.

Oxidation. Other types of degradation occur if cellulose is treated with oxygen in strongly alkaline solution or with a variety of oxidizing agents over a wide range of *p*H. The chemical mechanisms of these reactions, which are not as yet completely understood, are discussed in detail in Section I, 3 of this chapter. Typical possibilities for the primary attack are formulated below:



As a consequence of either of these types of reactions, the glucosidic bond will be weakened so that very mild reagents will attack it and cause a shortening of the average chain length. In these cases, however, the newly

[1] K. Freudenberg and W. Kuhn, *Ber.*, **65B**, 484 (1932).

[2] W. N. Haworth, *The Constitution of Sugars.* Edward Arnold, London, 1929.

[3] E. Heuser in H. Gilman, *Organic Chemistry.* John Wiley, New York, 1938.

[4] P. Karrer, *Polymere Kohlenhydrate.* Akademische Verlagsgesellschaft m. b. H., Leipzig, 1925.

[5] F. Klages, *Ber.*, **65B**, 302 (1932).

[6] K. H. Meyer, *High Polymers*, Vol. IV, *Natural and Synthetic High Polymers.* Interscience, New York 1942.

produced end groups have different structures than the normal glucose residues of the chains.

It is not immediately evident that oxidation at position 6 to a carboxyl would weaken the structure, but it is an established fact that alginic and pectic acids, containing very similar groupings, are quite unstable to alkali.

Other Degradation Reactions. Cellulose is also degraded by heating with water under pressure, by dry distillation, and by certain enzymes. However, all of these processes presumably occur under uncontrollable or complicated conditions, and any attempt at theoretical interpretations of them would meet with considerable difficulty at this time. Accordingly, the present theoretical approach is limited to considerations of only the hydrolytic and oxidative types of degradation.

Hydrolytic cleavage of cellulose is usually carried out in dilute solutions and, if the cellulose is highly swollen, the reaction mixture approaches, to a certain extent, the conditions of a homogeneous system. Degradation of alkali cellulose by oxygen, on the other hand, usually occurs in the wet fiber and hence shows more of the properties of a heterogeneous system, in which a swollen gel reacts with a substance which is dissolved in the swelling agent. There have been many experimental investigations involving both the hydrolytic and the oxidative types of cleavage, but the majority of them have been for technical purposes so that definite reproducible data on the rate of these two reactions under different experimental conditions are not abundant. There are, however, sufficient approximate data for consideration of the quantitative mechanism of the hydrolysis in a homogeneous system. It may be appropriate, therefore, to present the formulas which describe the cleavage of cellulose in homogeneous and heterogeneous systems, and then to mention briefly the experiments available to check the validity of these computations.

(*b*) *Theory for Degradation Reactions*

The earliest investigations of the degradation of cellulose and starch were made by Meyer, Hopff, and Mark,[7] and Freudenberg, Kuhn, and collaborators.[1, 8–11] The chief aim of these studies was to find out whether or not the bonds between consecutive glucose units were of the covalent

[7] K. H. Meyer, H. Hopff, and H. Mark, *Ber.*, **62B**, 1103 (1929).

[8] K. Freudenberg and E. Braun, *Ann.*, **460**, 288 (1928).

[9] K. Freudenberg, W. Kuhn, W. Dürr, F. Bolz, and G. Steinbrunn, *Ber.*, **63B**, 1510 (1930).

[10] W. Kuhn, *Ber.*, **63B**, 1503 (1930).

[11] W. Kuhn, *Z. physik. Chem.*, **A159**, 368 (1932).

type. It was found that the activation energy necessary to split these bonds was of the order of magnitude of 28,000 calories, and, hence, was comparable with the activation energy of normal covalent bonds. No attempts were made to draw any far-reaching conclusions about the kinetics of the degradation or the molecular distribution of the degraded material at any given time, although the formulas derived by Kuhn contained some information in this direction.

In later work the molecular distribution has been obtained mathematically by two methods: (a) a kinetic approach and (b) a statistical or probability approach. The kinetic method consists of setting up a differential equation, the terms of which express the rate of appearance and disappearance of each molecular species in the degrading mixture. This equation must then be integrated using the boundary conditions imposed by the assumptions made about the degradation process. This method is applicable to all possible degradation processes if the integration and evaluation of constants can be performed. The statistical method consists of assigning a probability of breaking to each bond in the degrading mixture and calculating the amount of each species in the resulting polymer system. The usefulness of this method is limited by the fact that calculations have been performed successfully for only the simplest degradation processes. These two methods yield identical expressions for the molecular distributions in the cases for which both types of calculations have been performed successfully.

Three distinct cases have been considered in an attempt to obtain a complete kinetic picture of the degradation process:

I. *Degradation of chains of infinite length if all bonds split with the same probability* (*break at the same rate*) (Kuhn,[10, 11] Olmstead[12]).

II. *Degradation of chains with finite, uniform length if all bonds split with the same probability* (Durfee and Kertesz,[13] Montroll,[14, 15] Olmstead,[12] Simha,[15, 16, 17] Sakurada and Okamura[18]).

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[12] Dr. P. S. Olmstead of the Research Laboratories of the Bell Telephone Company has kindly informed the authors of an article that he has worked out but not published on a statistical theory of degradation processes. The authors are very much indebted to Dr. Olmstead for this communication and, with his kind permission, are including in this report some expressions derived by him, such as equations (14), (15), (16), and (17).

[13] W. H. Durfee and Z. I. Kertesz, *J. Am. Chem. Soc.*, **62**, 1196 (1940).

[14] E. W. Montroll, *J. Am. Chem. Soc.*, **63**, 1215 (1941).

[15] E. W. Montroll and R. Simha, *J. Chem. Phys.*, **8**, 721 (1940).

[16] H. Mark and R. Simha, *Trans. Faraday Soc.*, **36**, 611 (1940).

[17] R. Simha, *J. Applied Phys.*, **12**, 569 (1941).

[18] I. Sakurada and S. Okamura, *Z. physik. Chem.*, **A187**, 289 (1940).

III. *Degradation of chains with finite length having a certain chain-length distribution if all bonds split with different probabilities* (Debye,[19] Simha[17]).

All three of these cases have been treated by the kinetic method and Cases I and II have also been treated by the statistical method.

The random degradation of infinite chains I can be treated as a limiting case of II and, therefore, it is desirable to present the results of the latter treatment here.

Initial Molecules of Uniform Chain Length. Assume an idealized long-chain polymer system, such as cellulose or one of its derivatives, containing N_0 polymer molecules each of which is composed of $(p + 1)$ monomer units linked by p bonds. The total number of monomer units present is $N_0(p + 1)$. Let this system be depolymerized to a degree α, which is defined as the average fraction of bonds (r) broken in each chain molecule, that is, $\alpha = \frac{r}{p}$, and which, therefore, is equal to the chance of any one bond breaking. The probability of one particular bond being left unbroken is $(1 - \alpha)$ and the chance of a chain with p bonds escaping degradation is $(1 - \alpha)^p$ The fraction of the monomer units which are left in the undegraded chains of $(p + 1)$ units is, therefore,

$$F_{p+1(p,\alpha)} = (1 - \alpha)^p \tag{1}$$

The fraction of monomer units in the degradation product molecules of j-units can be shown to be:

$$F_{j(p,\alpha)} = \frac{\alpha j(1 - \alpha)^{j-1}}{p + 1} [2 + (p - j)\alpha] \qquad j \leq p \tag{2}$$

This fraction can also be expressed as:

$$F_{j(p,\alpha)} = \frac{jN_{j(p,\alpha)}}{N_0(p + 1)} \tag{3}$$

where $N_{j(p,\alpha)}$ is the number of j-mers in the system after an average of r bonds per molecule have been broken in N_0 molecules of $(p + 1)$ monomer units. Then from (2) and (3)

$$N_{j(p,\alpha)} = N_0\alpha(1 - \alpha)^{j-1} [2 + (p - j)\alpha] \qquad j \leq p \tag{4}$$

Similarly from (1) and (3):

$$N_{p+1,\alpha} = N_0 (1 - \alpha)^p \tag{5}$$

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[19] H. Mark and R. Raff, *High Polymers*, Vol. III, *High Polymeric Reactions*. Interscience, New York, 1941.

Simha, in a more general treatment starting with the rate equations for each degrading species, found that his result reduced to (4) and (5) for random chain breaking in an idealized uniform-chain-length polymer. By using the following equation:

$$\alpha = 1 - e^{-kt} \tag{6}$$

which shows the dependence of α on time (t), Simha obtained:

$$N_{j,t} = N_0 e^{-kt(j-1)} (1 - e^{-kt}) [2 + (p - j)(1 - e^{-kt})] \qquad j \leq p \tag{7}$$

and:

$$N_{p+1,t} = N_0 e^{-ktp} \tag{8}$$

Equations (7) and (8), which are equivalent to (4) and (5), give the number distribution at any instant in the degradation process. The number-fraction distribution can be obtained from (7) and (8), or (4) and (5), after a summation process.

Distribution curves, such as those which may be calculated from equations (1), (2), (4), (5), (7), and (8), give a valuable picture of a polymer system. However, average molecular weights, which are much less informative, are frequently used to describe such systems, because of their greater simplicity. It has been shown by Kraemer and Lansing[20, 21] that the molecular weight obtained by methods which depend on the counting of molecules, such as osmotic-pressure or vapor-pressure methods and chemical analysis, is the *number-average* molecular weight:

$$\mathbf{M}_n = \frac{\Sigma M_j N_j}{\Sigma N_j} \tag{9}$$

where M_j is the molecular weight of the j-th species of which there are N_j individuals. Methods depending on the weights of molecules, such as those which measure diffusion or viscosity, give the *weight-average* molecular weight:

$$\mathbf{M}_w = \frac{\Sigma N_j M_j^2}{\Sigma N_j M_j} \tag{10}$$

For a homogeneous material $\mathbf{M}_n = \mathbf{M}_w$ but for a polymolecular system $\mathbf{M}_n < \mathbf{M}_w$. The difference between the average molecular weights increases as the range of chain lengths in the system increases. Montroll and Simha[15] and Olmstead[12] expressed the average molecular weights of the entire degraded polymer system as:

$$\mathbf{M}_{n(p,\alpha)} = M_0 \frac{p + 1}{1 + \alpha p} \tag{11}$$

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[20] W. D. Lansing and E. O. Kraemer, *J. Am. Chem. Soc.*, **57**, 1369 (1935).

[21] E. O. Kraemer, *J. Franklin Inst.*, **231**, 1 (1941).

and

$$\mathbf{M}_{w(p,\alpha)} = M_0 \frac{\alpha^2(1+p) + 2(1-\alpha)[(1-\alpha)^{p+1} + \alpha(p+1) - 1]}{\alpha^2(1+p)} \quad (12)$$

where M_0 is the weight of the monomer unit. Equation (11) can be converted using equation (6) to show the time dependence of the *number-average* molecular weight resulting from a degradation process:

$$\left(\frac{\mathbf{M}_{n-1}}{M_0}\right) \Big/ \frac{\mathbf{M}_n}{M_0} = \frac{p}{p+1} e^{-kt} \quad (13)$$

This is the relation found by Wolfrom, Sowden, and Lassettre.[22]

The values of α and p may be determined from the average molecular weight relations (11) and (12) by measuring experimentally $\mathbf{M}_n$ or $\mathbf{M}_w$ of the original and of the degraded material. If these values are known, equations (1) through (8) may be applied to obtain the various distribution curves.

None of the equations given in the preceding discussion have described a specific fraction of the degraded polymer. Frequently, however, experimental measurements on the higher-molecular-weight fractions are of greater value than those on the degraded system as a whole. For such fractions the following expressions, derived by Olmstead,[12] are applicable:

Weight fraction of all molecules with lengths greater than j:

$$F_{(>j)p,\alpha} = \left[1 + \frac{\alpha j(p-j)}{1+p}\right](1-\alpha)^j \qquad 0 \le j \le p \quad (14)$$

Number fraction of all molecules of lengths greater than j:

$$f_{(>j)p,\alpha} = \left[1 - \frac{\alpha j}{\alpha p + 1}\right](1-\alpha)^j \qquad 0 \le j \le p \quad (15)$$

Weight-average molecular weight of the fraction containing all molecules of lengths greater than j:

$$\mathbf{M}_{w(>j)} = M_0 j + M_0 \left[\frac{\alpha(1+p-j)[2+\alpha(j-1)] - 2(1-\alpha)[1-(1-\alpha)^{1+p-j}]}{\alpha^2[1+p+\alpha j(p-j)]}\right] \quad 0 \le j \le p \quad (16)$$

Number-average molecular weight of the fraction containing all molecules of lengths greater than j:

$$\mathbf{M}_{n(>j)} = M_0\left[j + \frac{1+p-j}{1+\alpha(p-j)}\right] \qquad 0 \le j \le p \quad (17)$$

[22] M. L. Wolfrom, J. C. Sowden, and E. N. Lassettre, *J. Am. Chem. Soc.*, **61**, 1072 (1939).

A number of experiments with cellulose acetate and methylcellulose carried out by Mark and Simha,[16] and Wolfrom and collaborators[22, 23] seem to be in fair agreement with the relations for random degradation of finite, uniform chains. However, detailed studies including complete distribution curves at various stages of the degradation are necessary to establish the theory.

A simplification of equation (2) is obtained if p is very large compared to j. Such a condition approaches the case of random degradation of infinitely long chains (I). If p is of the order of 500, which corresponds to a fairly high polymeric material, and if only the later stages of degradation (α approaching unity) are considered, so that only monomers, dimers, trimers, and the next few species are left ($j = 1, 2, 3 \ldots$), equation (2) becomes

$$N_j = N_0(p + 1)(1 - \alpha)^{j-1}\,\alpha^2 \tag{18}$$

In this expression $N_0(p + 1)$ is the number of monomer units originally present and N is the number of degradation products composed of j monomers. This equation has been derived by Kuhn,[10, 11] and is in agreement with measurements of Freudenberg and his coworkers[1, 8, 9] on the hydrolysis of cellulose by mineral acids.

Initial Molecules of Definite Chain-Length Distribution. The degradation of polymolecular systems containing molecules of various chain lengths, if all bonds are broken with different probabilities (III), has been treated by Debye[19] and Simha.[17] Simha's treatment starts with the rate equations for each degrading species. The general solution of such equations has the form

$$\begin{aligned} N_{(j,\,t)} = {} & h_j a_{j,j} \exp.\ [-\sum_{1}^{j-1} k(i, j)t] \\ & + h_{j+1}\, a_{j,j+1} \exp.\ [-\sum_{1}^{j} k(i, j+1)t] + \ldots\ldots \\ & + h_{p+1}\, a_{j,\,p+1} \exp.\ [-\sum_{1}^{p} k(i, p+1)t] \end{aligned} \tag{19}$$

This relation gives the number N_j of molecules of each individual polymer as a function of time and of the different individual rate constants $k(i, j)$. The first subscript (i) gives the sequence number of the respective bond in the molecule and the second (j) gives the number of monomer units in the molecule. When k is dependent on j (independent of i), all bonds

[23] M. L. Wolfrom, D. R. Myers, and E. N. Lassettre, *J. Am. Chem. Soc.*, 61, 2172 (1939).

in each molecule are opened at the same rate but the absolute value of k depends on the length of the chain; when k is dependent on i (independent of j), all chains regardless of length behave identically but the individual bonds react differently; for example, those in the middle of the chain react at a different rate than those at the ends. If k is independent of i and j, all bonds, regardless of location in long or short chains, react identically.

Equation (19) is much too general and complicated to be applied to any specific system. However, in systems approaching homogeneous conditions, (19) reduces to (7) and (8) for uniform finite chains (II) and to (18) for infinite chains (I). In considering polymolecular systems, that is, those containing a number of molecular species as most polymer systems actually do, it is necessary to introduce assumptions as to the reactivities of the different bonds. There are certain experimental data indicating that thermal degradation of polyhydrocarbons, such as rubber, polystyrene, or polyvinyl derivatives, tends to occur at the end bonds. This apparent "evaporation" of monomer makes it seem that the probability of the end bonds breaking is somewhat greater than that of the central bonds. It is possible that the high-temperature degradation of cellulose during the cooking of wood chips and the stabilization of nitrocellulose under pressure occurs to some extent as a reaction of this type. There are at present no experimental data to prove or disprove such an assumption.

The solutions of equation (19) for such systems, where

$$k(1, j) = k(j - 1, j) = k \text{ and all other } k(i, j) = 0$$

have been discussed by Chalmers,[24] Dostal and Mark,[25] and Simha.[17] They show that the original material disappears gradually according to N_0e^{-kt}, the intermediate products increase to a maximum concentration and then slowly disappear, while the amount of monomer increases asymptotically to $(p + 1)N_0$.

(c) *Comparison with Experimental Data*

The above discussion and equations outline the present possibilities of investigating quantitatively the course of high-polymeric degradation reactions. A comparison of the theories represented by these equations with experimental data available can best be obtained graphically.

Theoretical Results. The chief feature of the degradation reaction starting with a uniform polymer (for example, with a certain frac-

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[24] W. Chalmers, *J. Am. Chem. Soc.*, **56**, 912 (1934).

[25] H. Dostal and H. Mark, *Z. physik. Chem.*, **B29**, 299 (1935).

tion of cellulose acetate) is the initial broadening of the molecular-size distribution curve. The distribution curve for the depolymerized material attains the greatest half-breadth[26] when the average molecular size is reduced to approximately one-half of the original. For a material of initial degree of polymerization (D.P.) of 350 (Fig. 4) this occurs at the stage of degradation $\alpha = 0.003$ Thirty-seven per cent of the monomer units then remain in the unattacked material (Fig. 5) so the distribution curve of the entire system (degraded portion plus the original) consists of the broad curve of the degraded portion plus the discontinuity due to the remaining

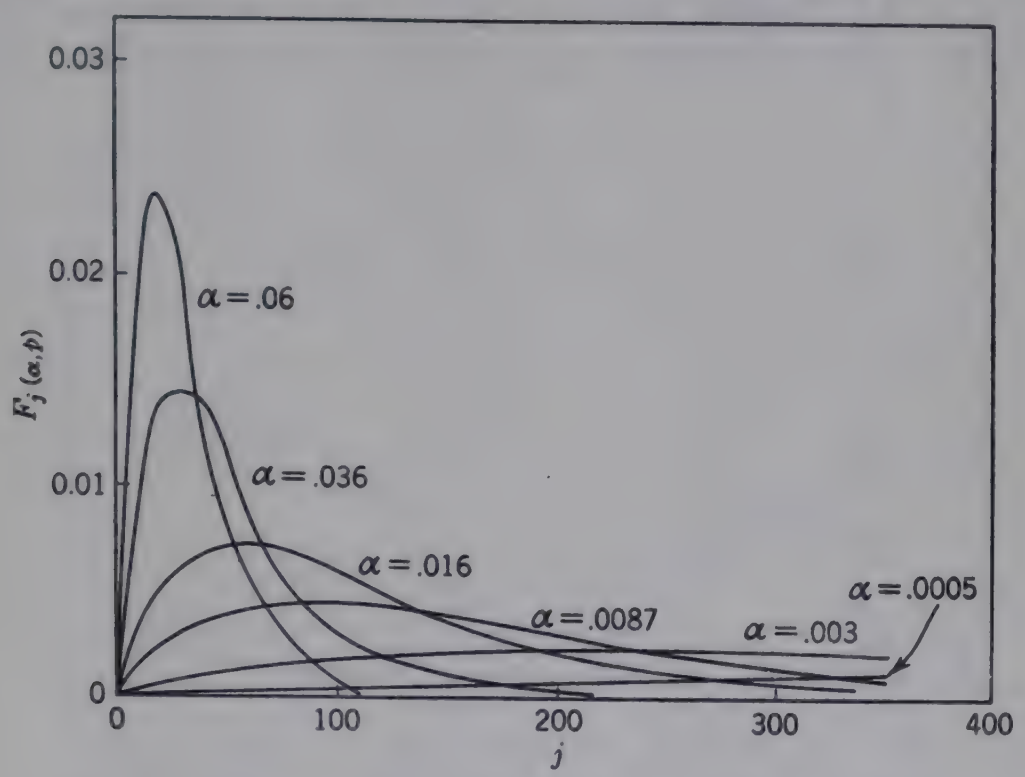

FIG. 4.—WEIGHT FRACTION OF MONOMER UNITS EXISTING AS COMPONENTS OF j-MERS FOR VARIOUS α'S IN A SYSTEM THAT ORIGINALLY CONTAINED ONLY POLYMERS OF 350 UNITS ($p + 1 = 350$).

Curves are calculated from equation (2).

original material. The material becomes more and more homogeneous as the degradation proceeds, because of the accumulation of the shorter chains and the disappearance of the original material, until all the chains are reduced to monomer units and a completely homogeneous system is obtained.

The chain-length distribution curves obtained from equation (2) are given in Figure 4. It is assumed that the starting material is an ideally homogeneous polymer containing 350 monomer units ($p + 1 = 350$). The curves give the weight fractions of the total monomer units present in

[26] Half-breadth is defined as the width of the curve at half its maximum height.

the various j-mers for various degrees of depolymerization α. The fractions of the total monomers remaining as undegraded original polymer ($p + 1 = 350$) at these various stages cannot be readily represented in Figure 4, but are given in Figure 5 (from equation (1)). The fraction given by the ordinate for any α in Figure 5 is equal to one minus the sum of all the ordinates under the corresponding α curve of Figure 4. Thus, both Figures 4 and 5 are required to represent the complete system.

It can be seen from Figure 4 that in the early stages of the degradation (low values of α) the distribution curves for the degraded material are very broad, but as the reaction proceeds the degraded material becomes more homogeneous. For values of α appreciably greater than 0.0087 (when 5%

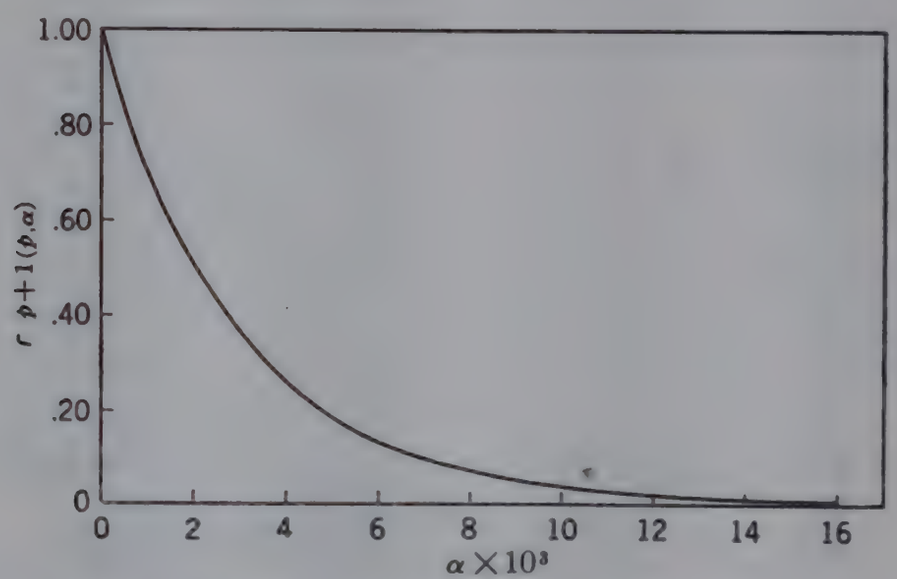

FIG. 5.—WEIGHT FRACTION OF MONOMER UNITS REMAINING IN THE ORIGINAL POLYMER ($p + 1 = 350$) AT VARIOUS DEGREES OF DEPOLYMERIZATION α.

Curves are calculated from equation (1).

of the total monomer units remain in the undegraded polymer) the amount of undegraded material becomes negligible and the distribution curve for the entire system approaches that given by the curves for the higher values of α, that is, $\alpha = 0.036$, or $\alpha = 0.06$.

The curves of Figure 6 show the same change in distribution starting with a polymer with the same average degree of polymerization ($p + 1 = 350$) but having a Gaussian distribution of chain length. The distribution of the original polymer is given by the curve $\alpha = 0$. The other curves represent the weight fractions of the monomer units existing as components of the various j-mers for various degrees of depolymerization α. The moderately degraded products again vary widely in chain length (chiefly because

of the remaining portion of the peak due to the unattacked original material) while the highly degraded ones become more and more homogeneous.

Experimental Results. Figure 7 shows an experimentally determined series of chain-length distribution curves for cellulose acetates (39.3% acetyl content) according to Mark and Simha.[16] Curve 1 represents the original material having an average D.P. of approximately 350 and a distribution which deviates but little from the Gaussian form (compare Fig. 3). Curves 2, 3, and 4 are characteristic for three different stages of cleavage with values of D.P. of 158, 100, and 54, respectively. The general

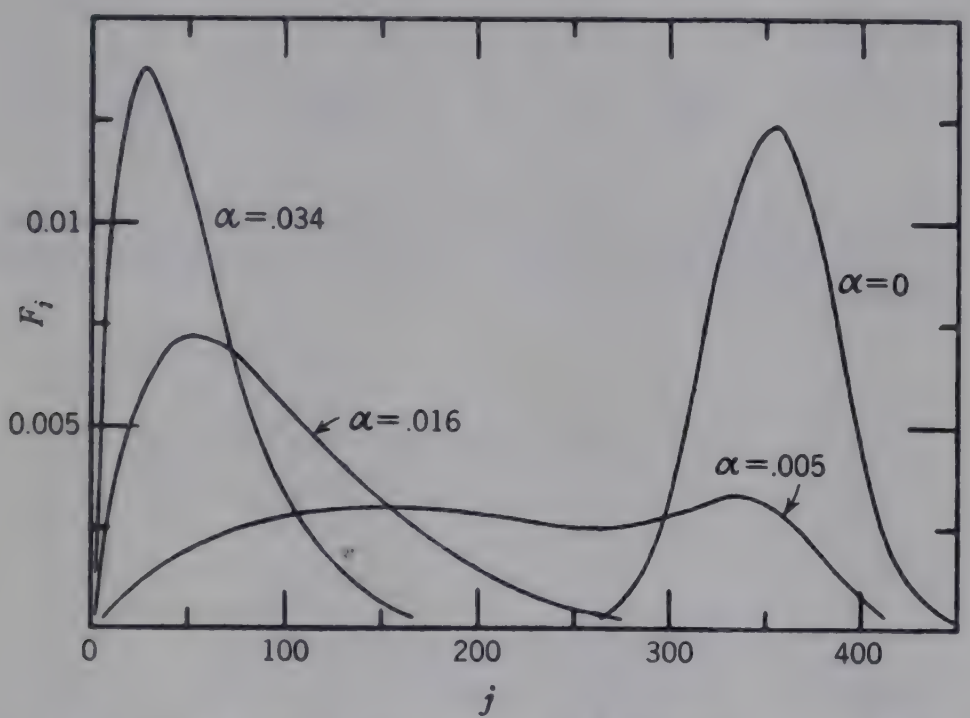

FIG. 6.—WEIGHT FRACTION OF MONOMER UNITS EXISTING AS COMPONENTS OF j-MERS FOR VARIOUS α'S IN A SYSTEM THAT ORIGINALLY HAD A NORMAL (GAUSSIAN) DISTRIBUTION OF MOLECULAR SIZES (AVERAGE $\bar{p} + 1 = 350$) (MONTROLL[14]).

form of these curves resembles that of Figure 6 which represents the assumption of random breaking of all reactive bonds. It should be noted, however, that a pronounced peak at $j = 350$ would be expected for the sample D.P. = 158.

Experimental chain-length distribution data obtained from the degradation of various kinds of cellulose under different conditions[27] are given in Figure 8. Curve 1 represents the weight distribution for a purified cotton linters sample such as is used for high-grade viscose rayon yarns; Curve 2 represents a wood pulp (91.5% alpha-cellulose). Curve 2a is for the same

[27] H. Mark, *Paper Trade J.*, **113**, 34 (July 17, 1941).

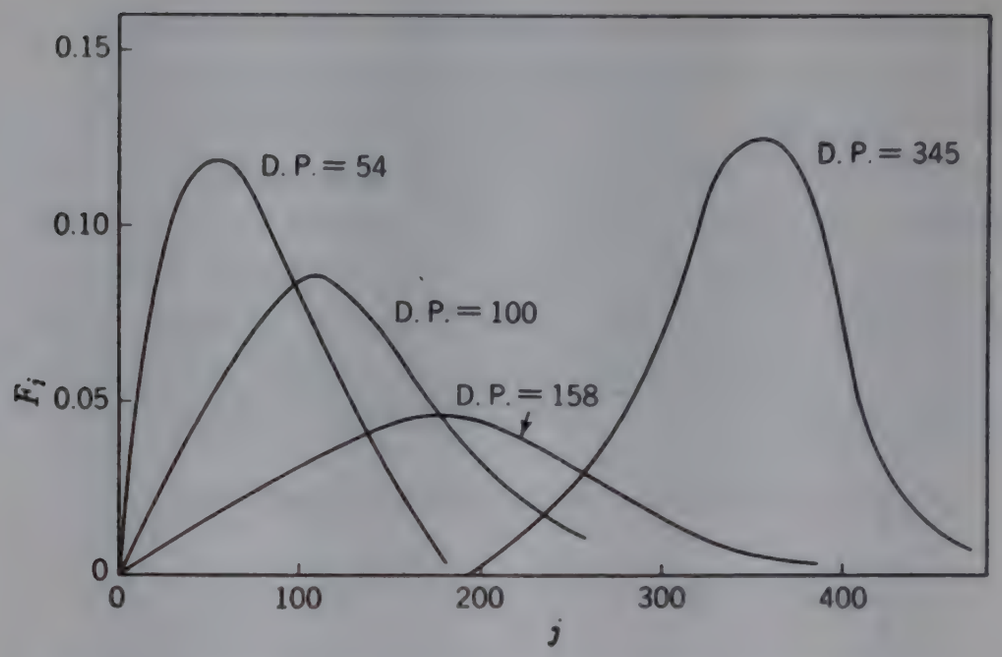

FIG. 7.—WEIGHT FRACTION OF MONOMER UNITS EXISTING AS COMPONENTS OF j-MERS IN CELLULOSE ACETATE FRACTIONS (MARK AND SIMHA[16]).

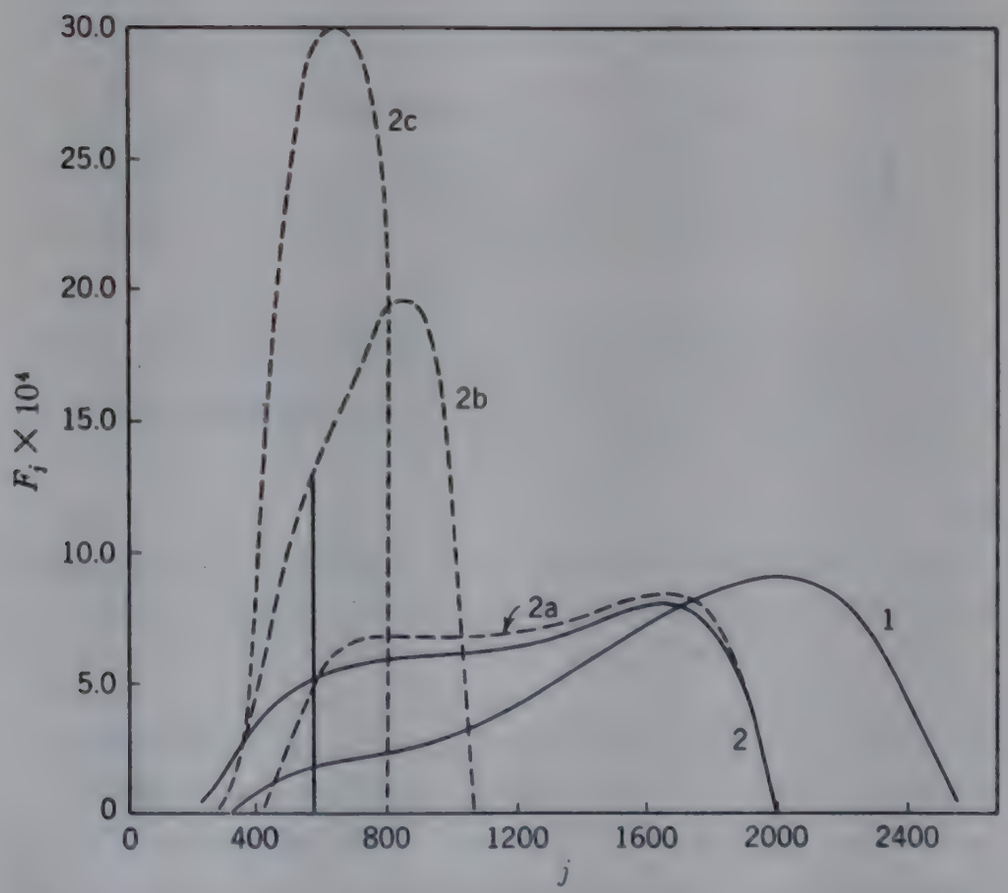

FIG. 8.—WEIGHT FRACTION OF MONOMER UNITS EXISTING AS COMPONENTS OF j-MERS IN VARIOUS CELLULOSE SAMPLES (MARK[27]).

pulp after steeping in 17% caustic soda. When this pulp was converted to alkali cellulose and aged 20 and 70 hours, Curves 2b and 2c, respectively, were obtained. The first three of these curves are typical for highly purified and mildly degraded cellulose specimens while the latter two represent the more highly degraded types. These curves have the general form predicted by the theoretical considerations and found in other degradation experiments, but, since the degradations were carried out under the conditions used in the industrial processes, which are neither truly homogeneous nor truly

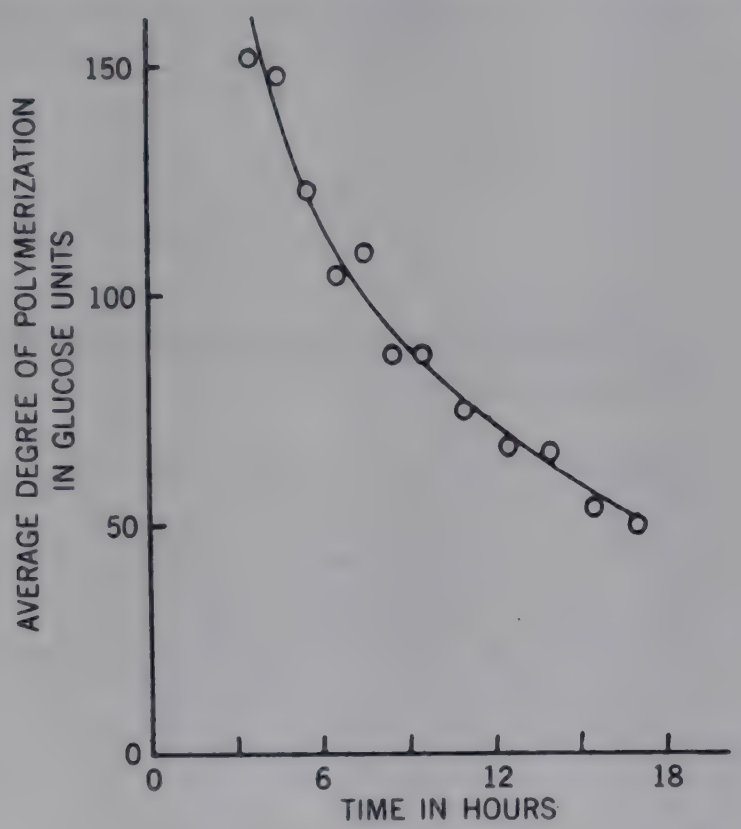

FIG. 9.—RATE OF CHANGE OF AVERAGE DEGREE OF POLYMERIZATION (D.P.) OF METHYLATED CELLULOSE (2.3% IN FUMING HCl AT 0°C.) (WOLFROM, SOWDEN, AND LASSETTRE[22]).

heterogeneous, the curves can only be taken as a qualitative support for the general theory without permitting any detailed quantitative conclusions.

Figure 9, obtained by Wolfrom and his coworkers,[22, 23] shows the rate of change of the average D.P. of methylated cellulose as a 2.3% solution in fuming hydrochloric acid at 0°C. The rate constant of hydrolysis, $k = 1.02 \times 10^{-3}$ hr.$^{-1}$ or $k = 2.89 \times 10^{-7}$ sec.$^{-1}$, can be obtained from these data using equations (5) and (7). Amylose hydrolyzes[7] in dilute sulfuric acid at 70°C. with a constant $k = 1.0 \times 10^{-3}$ sec.$^{-1}$; cellulose[8, 9] at 30°C. with a rate $k = 3.2 \times 10^{-4}$ sec.$^{-1}$.

The activation energies and the frequency constant for the breaking of different α- and β-glucosidic bonds can be calculated from the temperature dependence of the corresponding k values. Table 1 gives the results of

TABLE 1

SOME ACTIVATION ENERGIES AND FREQUENCY CONSTANTS FOR THE HYDROLYSIS OF GLUCOSIDIC BONDS

Glucosidic bond in	Action or frequency constant $\times 10^{-16}$	Activation energy in cal. per mole of the bond
Maltose	70	29,600
Amylose	50	29,000
Cellobiose	1300	31,000
Cellulose	4	28,100

these calculations by Freudenberg, Kuhn, and their collaborators[1, 8, 9, 10] and by Meyer, Hopff, and Mark.[7]

The following conclusions may be drawn from the work to date:

1. The general theory of the degradation of linear polymers, such as cellulose and its derivatives, has been developed to a fair degree.
2. The over-all rate of the degradation and the distribution curves of the degraded products as far as they have been determined are in qualitative agreement with the predictions of the theory.
3. No conclusive experiments are yet available to check the theoretical relations in detail.

2. Hydrocellulose

HENRY A. RUTHERFORD AND MILTON HARRIS

Cellulose is readily degraded by hydrolytic or oxidative processes, the former usually being accomplished by treatment with acids and the latter by oxidizing agents in acid, neutral, or alkaline solutions. The degraded, insoluble portion of the cellulose is usually referred to as "hydrocellulose" or "oxycellulose" depending on whether it is prepared by hydrolytic or oxidative treatment. Oxycellulose will be described in the next section of this chapter. Both discussions are for the most part limited to

the products formed in the early stages of degradation since these are of the greatest commercial and practical interest, and have received more attention than the highly degraded materials.

(a) *Preparation of Hydrocellulose*

Treatment of purified cellulose with cold solutions of mineral acids results in a slow hydrolysis of the material and, if the reaction is allowed to proceed far enough, glucose and a small amount of its acid decomposition products are the final products obtained. The hydrolytic process, however, does not take place in a uniform manner, and, if the reaction is stopped at any time, the partially hydrolyzed cellulose may be divided into a number of fractions, the molecular weights of which may vary between that of glucose and that of the original material itself. A wide variety of hydrocelluloses, existing as fibers or as powders, can thus be prepared at will depending upon conditions employed in the acid treatment.

Girard[1] was one of the earliest investigators to show that hydrocellulose could be prepared by a number of methods. He was able to produce a series of white, friable powders by immersion of cellulose in mineral acids, by the action of moist gaseous halogen acids, or by impregnating the fibers with solutions of certain organic acids and then heating the materials in closed vessels at 100°C. Organic acids were found to produce tendering of the cellulose at a much slower rate than mineral acids.[2]

During the thirty-five years subsequent to Girard's work, there appeared a number of additional papers describing the preparation of hydrocellulose by the acidic modification of cellulose. A summary of the literature over this period has been made by Clifford.[3] Due to the different experimental conditions used by the various investigators, considerable variations in the properties of the modified cellulosic products were found, and controversies arose as to whether hydrocelluloses represented definite chemical substances corresponding to a definite state of degradation or whether they were simply mixtures of the degradative products of the original cellulose. For example, Hess and Wittelsbach[4] believed hydrocellulose to be a more or less homogeneous chemical individual, and sug-

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[1] A. Girard, *Compt. rend.*, **81**, 1105 (1875); **88**, 1322 (1879); *Ann. chim. phys.*, **24**, 337 (1881).

[2] H. J. Henk, *Monatschr. Textil-Ind.*, **52**, 23 (1937); *Kunstseide u. Zellwolle*, **21**, 165 (1939).

[3] P. H. Clifford, *J. Textile Inst.*, **14**, T69 (1923).

[4] K. Hess and W. Wittelsbach, *Z. Elektrochem.*, **26**, 232 (1920).

gested a chemical formula for it. It is generally accepted at the present time, however, that degradation of cellulose by acids results in a cleavage of the glucosidic linkages with the formation of two new terminal residues, one characterized by the presence of a reducing hemiacetal group, the other by an extra hydroxyl group. The degraded material consists of a homologous series of celluloses in which the macromolecules may have arrangements similar to those in the original material but are nonhomogeneous in character and exhibit lower average molecular lengths than the original cellulose.

A different type of degradation may be obtained as indicated by the recent experiments of Ulmann and Hess,[5] who suggested that the action of gaseous or liquid hydrogen chloride on cellulose in the absence of water results in the formation of a water-soluble product with a hydrochloric acid content of about 25% and having a formula of $(C_6H_{10}O_5)_2 \cdot 3HCl$. The type of degradation obtained with either gaseous or liquid hydrochloric acid depends upon the amount of water present but the course of degradation appears to be similar with both reagents.

The factors influencing the rate of hydrocellulose formation have been investigated by Birtwell, Clibbens, and Geake[6] who were among the first to realize that the properties of hydrocelluloses are variable, and that complete loss of strength of cotton fibers does not correspond to a definite state of chemical degradation. They found that the rate of attack of the cellulose by acids was dependent on temperature, acid concentration, type of acid, and presence of neutral salts. On the basis of these experiments, they pointed out the necessity of carefully defining the conditions for the preparation of hydrocellulose to be used in experimental work and showed, for example, that two hydrocelluloses, having practically identical physical properties and viscosity characteristics, can be prepared at different times provided the conditions of the treatment used in the degradation are the same.

(*b*) *Properties of Hydrocellulose*

Most of the work that has been done in respect to the acid modification of cellulose indicates that this type of degradation is caused exclusively by hydrolysis of the 1,4-glucosidic linkages, the result of which is a shortening of the cellulose chain to produce fragments having lower aver-

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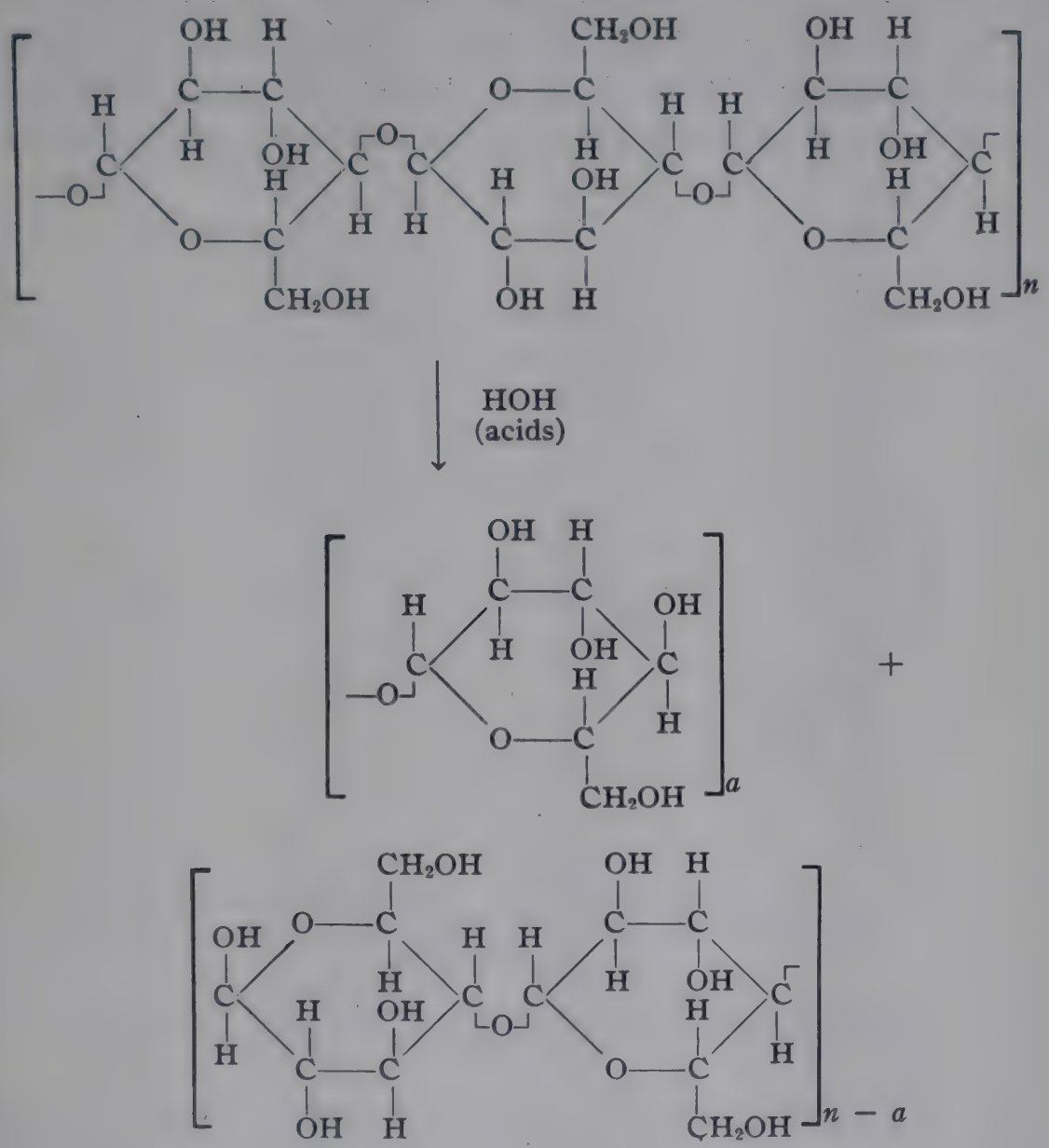
[5] K. Hess and M. Ulmann, *Ber.*, **74B,** 119 (1941); M. Ulmann and K. Hess, *Ber.*, **74B,** 136 (1941).

[6] C. Birtwell, D. A. Clibbens, and A. Geake, *J. Textile Inst.*, **17,** T145 (1926).

age molecular weights than that of the untreated cellulose.[7] The reaction may be represented by the following scheme:



It would be expected that the properties of cellulose would be profoundly altered by this type of cleavage and, indeed, this is shown to be true.

Two of the most characteristic changes which accompany the degra-

[7] See, for example: Wise,[8] Carrington, Haworth, Hirst, and Stacey,[9] Haworth, Peat, and Wilson,[10] Staudinger and Sorkin,[11] and Martin, Smith, Whistler, and Harris.[12]

[8] L. E. Wise, *Trans. Electrochem. Soc.*, preprint, 1938, 15 pp.

[9] H. C. Carrington, W. N. Haworth, E. L. Hirst, and M. Stacey, *J. Chem. Soc.*, **1939**, 1901.

[10] W. N. Haworth, S. Peat, and W. J. Wilson, *J. Chem. Soc.*, **1939**, 1903.

[11] H. Staudinger and M. Sorkin, *Ber.*, **70B**, 1565 (1937).

[12] A. R. Martin, L. Smith, R. L. Whistler, and M. Harris, *J. Research Natl. Bur. Standards*, **27**, 449 (1941); *Am. Dyestuff Reptr.*, **30**, 628 (1941).

dation of cellulose by acids are an increase in fluidity of a cuprammonium hydroxide solution of the material and a corresponding decrease in strength. Since both of these properties are dependent to a considerable extent upon the average molecular length of the cellulose molecules, it is not surprising that a definite relation between loss in strength and increase in fluidity is found. Such relationships in acid-modified celluloses have been frequently

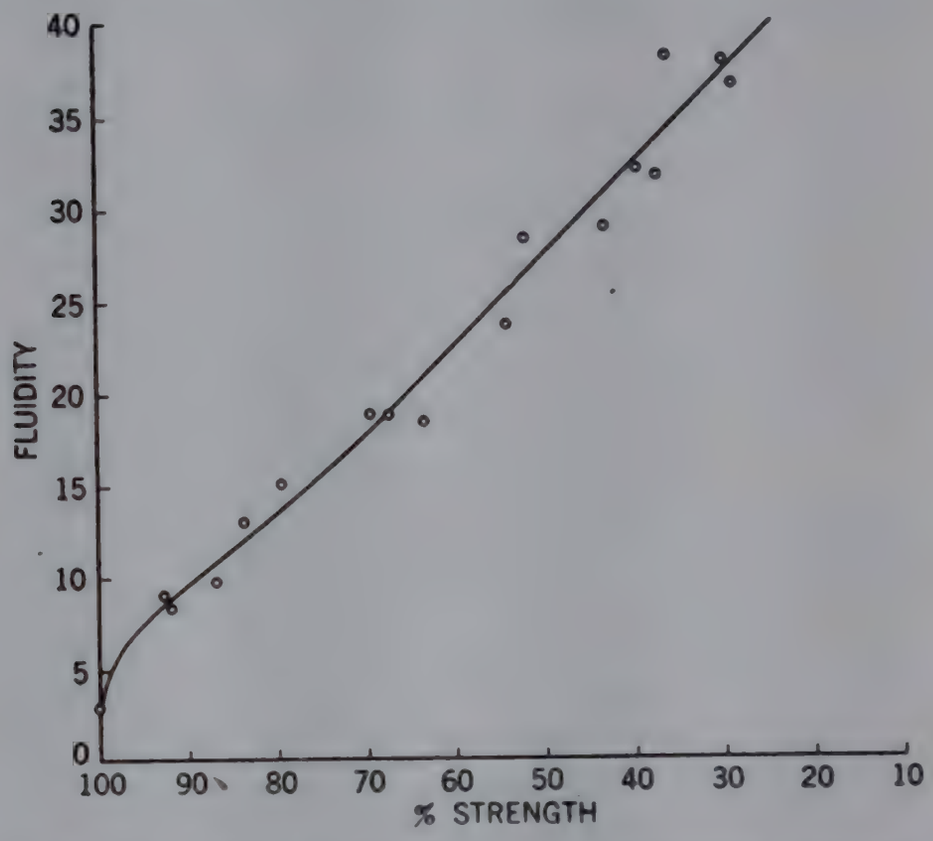


FIG. 10.—THE RELATION BETWEEN BREAKING STRENGTH AND FLUIDITY OF HYDROCELLULOSES (CLIBBENS AND RIDGE[14]).

demonstrated.[6, 13, 14, 15] Figure 10 emphasizes this relation. Since the data in Figure 10 were obtained on samples which had been treated under a variety of conditions, it can further be concluded that the changes are independent of the treatment. It should be pointed out, however, that this relationship would be expected to hold only when the cellulosic material is more or less uniformly degraded. Thus, highly localized attack on cellulosic fibers could result in a large loss of strength without an accompanying appreciable increase in fluidity.

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[13] F. D. Farrow and S. M. Neale, *J. Textile Inst.*, **15**, T157 (1924).

[14] D. A. Clibbens and B. P. Ridge, *J. Textile Inst.*, **19**, T389 (1928).

[15] R. T. Mease and L. F. Gleysteen, *J. Research Natl. Bur. Standards*, **27**, 543 (1941)

The relationship of tensile characteristics of hydrocelluloses to degree of polymerization (D.P.) or average molecular length is further demonstrated by the results of Staudinger, *et al.*,[16] shown in Figure 11. It was found that materials having D.P.'s of 200 to 250 (determined viscometrically) disintegrated on handling, while in the range of 250 to 700, the breaking strength and elongation increased with increase in D.P. Further increases beyond 700 resulted in only slight further changes in these properties.

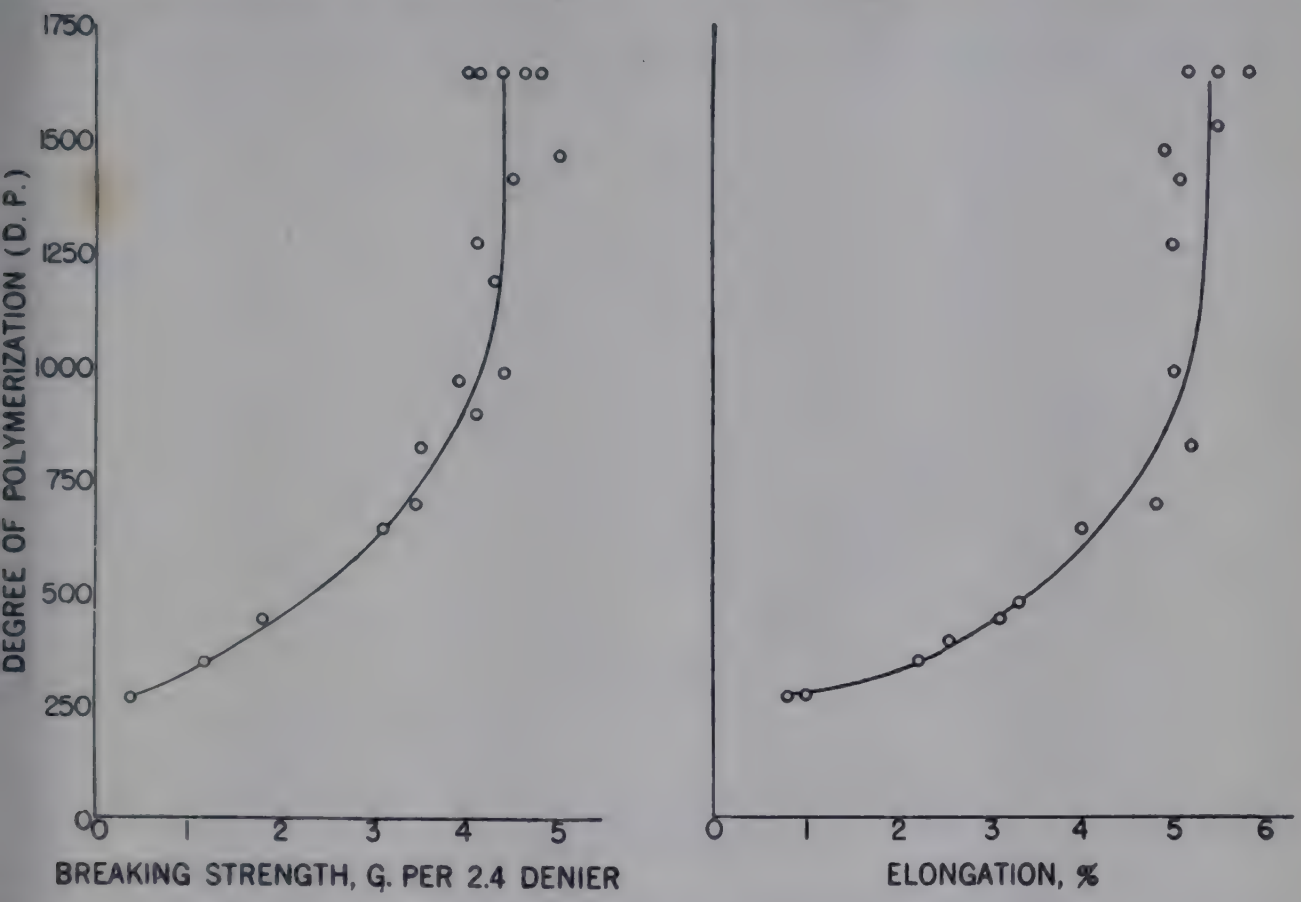

FIG. 11.—THE RELATIONSHIP OF STRENGTH AND ELONGATION TO DEGREE OF POLYMERIZATION (D.P.) OF COTTON FIBERS (STAUDINGER AND SORKIN[16]).

Another characteristic change which accompanies the formation of hydrocellulose is the increase in reducing properties, arising from the production of hemiacetal end groups. The presence of these groups is shown by the reducing action of hydrocellulose on copper (*e. g.*, Fehling's solution), ammoniacal silver nitrate,[17] and by reaction with phenylhydrazine,[18]

[16] H. Staudinger and M. Sorkin, *Ber.*, **70B**, 1565 (1937); H. Staudinger and J. Jurisch, *Zellwolle, Kunstseide, Seide*, **44**, 375 (1939); H. Staudinger and A. W. Sohn, *Ber.*, **72B**, 1709 (1939).

[17] G. Büttner and J. Neuman, *Z. angew. Chem.*, **21**, 2609 (1908).

[18] F. Müller, *Helv. Chim. Acta*, **22**, 217 (1939).

hydroxylamine,[19] Schiff's reagent,[19] and ethyl mercaptan.[20, 21] The number of these groups may be estimated by several methods (discussed in Section C of this chapter).

By comparison of the quantity of reducing end groups with the fluidities or viscosities of a series of hydrocelluloses, the validity of the mechanism for the acid cleavage of cellulose may be demonstrated. Such comparisons have been made by relating copper numbers to viscosity[6] as shown in

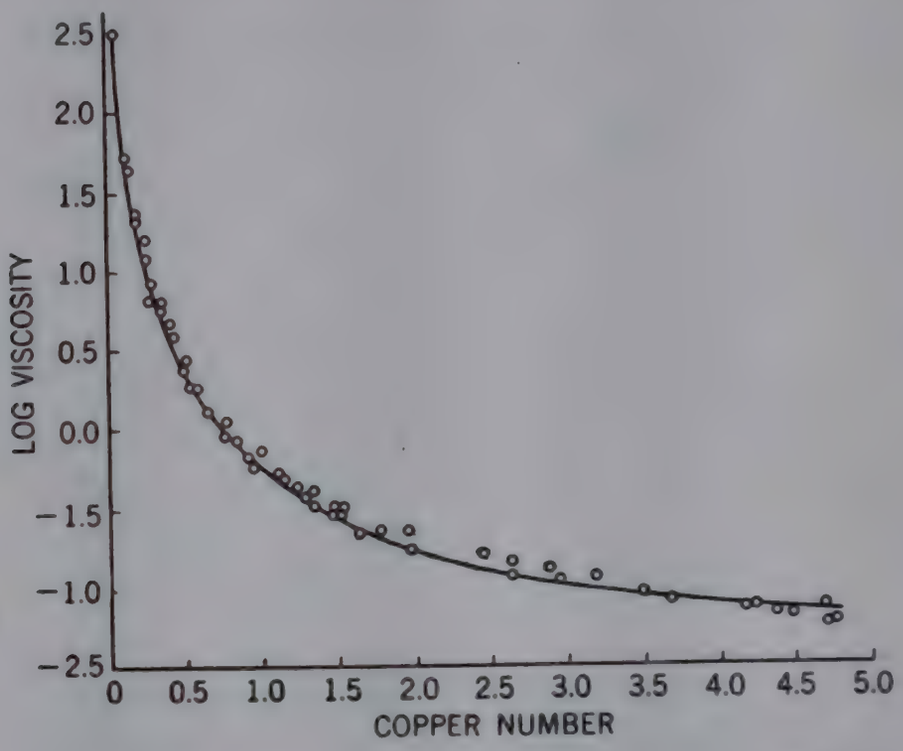

FIG. 12.—RELATION BETWEEN VISCOSITY AND COPPER NUMBER OF HYDROCELLULOSES (BIRTWELL, CLIBBENS, AND GEAKE[6]).

Figure 12, and more recently by relating the actual content of aldehydic groups to fluidity[12] as shown in Figure 13.

An examination of seventy different hydrocellulose samples prepared by a wide variety of acidic treatments[6] has shown that when the copper number lies within the limits of 0.3 and 4.0, its relationship to viscosity can be expressed by the equation $N_{Cu}V^2 = 2.6$ where N_{Cu} is the copper number and V is the logarithm of the relative viscosity. On the other hand, oxycelluloses which have copper numbers between the above limits do not follow this relationship and accordingly it has been suggested[6] that this

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[19] H. A. Rutherford, F. W. Minor, and M. Harris, unpublished data.
[20] M. L. Wolfrom and L. W. Georges, *J. Am. Chem. Soc.*, 59, 282 (1937).
[21] M. L. Wolfrom and J. C. Sowden, *J. Am. Chem. Soc.*, 60, 3009 (1938).

difference be used as a means of differentiating between these two types of modified celluloses.

The decrease in molecular size of cellulose during degradation with acids is accompanied by an increase in solubility, especially in alkaline solutions. However, even boiling water dissolves a fraction of hydrocellulose[22] which is higher in reducing power than the original hydrocellulose. When hot dilute solutions of alkalies are used, additional soluble decomposition

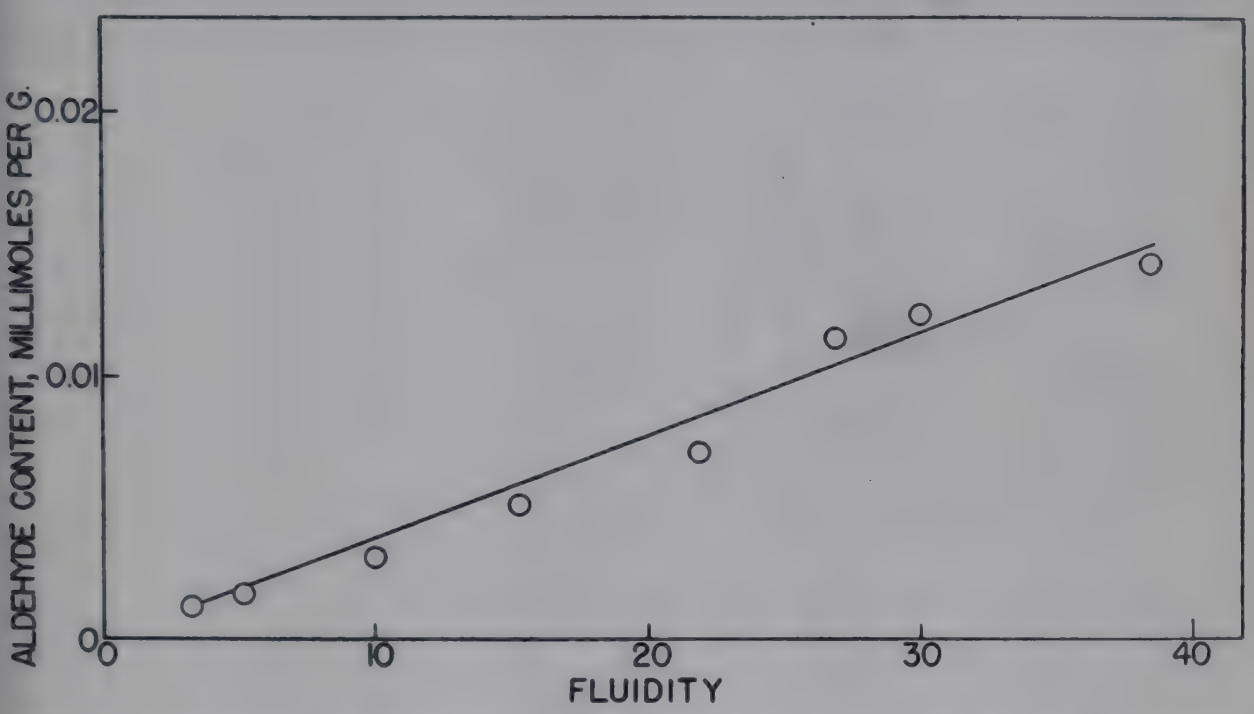

FIG. 13.—RELATION OF ALDEHYDIC CONTENT OF HYDROCELLULOSES TO FLUIDITY (MARTIN, SMITH, WHISTLER, AND HARRIS[12]).

products are obtained. The loss in weight, the effect on fluidity and breaking strength, and the change in copper number of hydrocelluloses on boiling in alkaline solutions has been rather extensively investigated.[14, 23–27] In general, it has been found that the reducing power of the hydrocellulose on treatment with hot alkali is decreased and may even fall to nearly zero without necessarily being accompanied by extensive weight losses. Some of the reducing power, however, is gained by the alkaline solution. Thus when some hydrocelluloses are treated with sodium hydroxide solutions,

[22] O. Hauser and H. Herzfeld, *Chem.-Ztg.*, **39**, 689 (1915).
[23] G. Witz, *Bull. soc. ind. Rouen*, **11**, 169 (1883).
[24] D. A. Clibbens, A. Geake, and B. P. Ridge, *J. Textile Inst.*, **18**, T277 (1927).
[25] C. Birtwell, D. A. Clibbens, and A. Geake, *J. Textile Inst.*, **19**, T349 (1928).
[26] G. F. Davidson, *J. Textile Inst.*, **25**, T174 (1934).
[27] G. F. Davidson, *J. Textile Inst.*, **27**, T112 (1936).

the reducing values of the extracts are rougnly constant at a copper number of 4, irrespective of the nature and extent of the acid attack; this relation, however, does not hold for celluloses which have been only slightly modified by the action of acids. The solubilities in alkali of hydrocelluloses appear to be related to the reducing power of the material; that is, hydrocelluloses of the same copper number have been shown to have the same solubility.[25] This relation is not the same for mercerized and unmercerized cotton; for

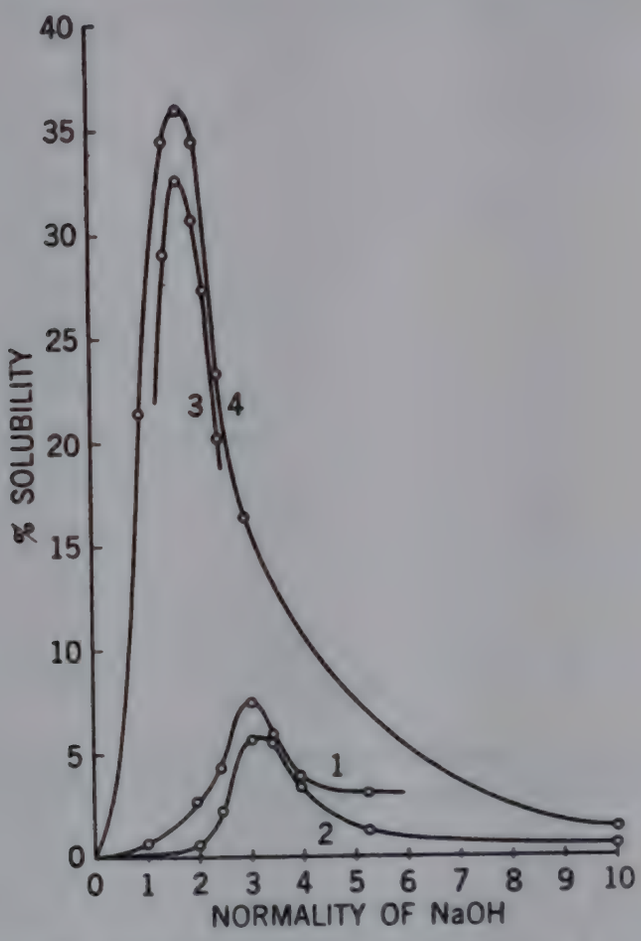

FIG. 14.—THE RELATION BETWEEN ALKALI CONCENTRATION AND SOLUBILITY OF HYDROCELLULOSE (BIRTWELL, CLIBBENS, AND GEAKE[25]).

Curve 2, a hydrocellulose having a copper number of 2.95.
Curve 3, a similar hydrocellulose after pretreatment with 10 *N* NaOH.

the same copper number, a hydrocellulose from the latter dissolves to a greater extent in alkaline solutions than one from the former.

At ordinary temperatures, the maximum solubility of hydrocellulose on treatment with any single solution occurs in 3 *N* sodium hydroxide, the solubility falling off rapidly from this point either with increasing or decreasing alkali concentration. However, if the material is first treated with a more concentrated caustic solution (6 *N* to 10 *N*), and the alkali then diluted by the addition of water, a larger percentage of the total modified

cellulose will dissolve than if a single solution is used. For example, Curve 2 in Figure 14 represents a single treatment of hydrocellulose with alkali; Curve 3 shows the effect on solubility of pretreatment of a similar hydrocellulose with 10 *N* NaOH in which the material is initially practically insoluble.

The effect of temperature on the solubility of hydrocellulose is shown in Figure 15. A maximum solubility is obtained with 3 *N* NaOH at 15°C.; the maximum is shifted to about 2.5 *N* at lower temperatures, the material being most soluble at −5°C., the lowest temperature used.[26]

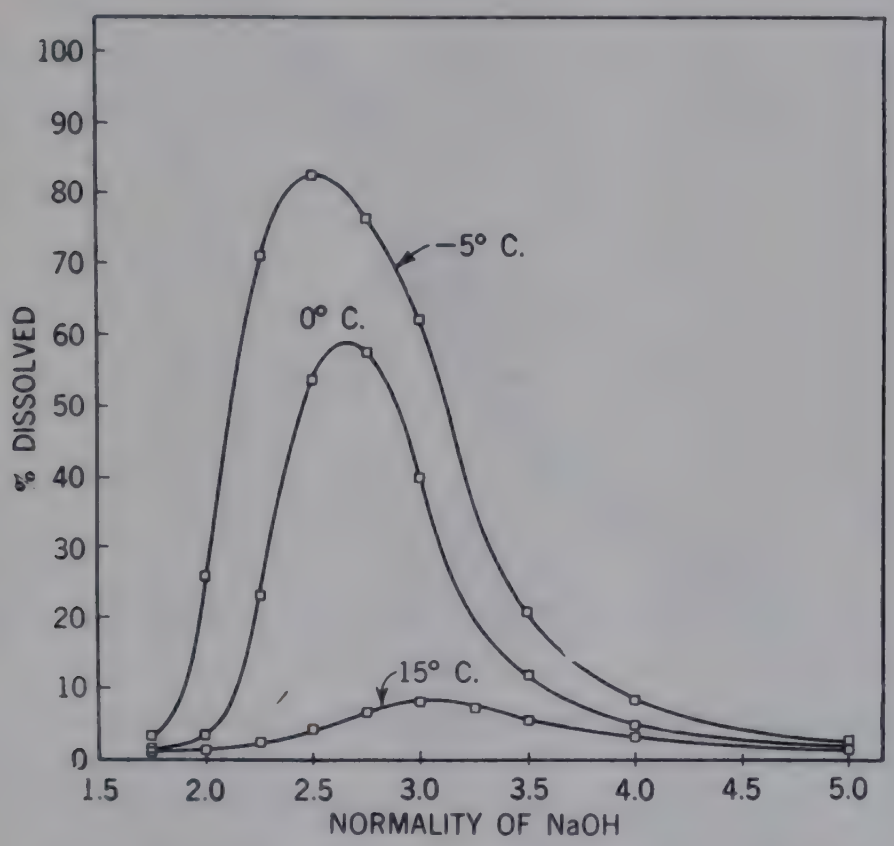

FIG. 15.—THE EFFECT OF TEMPERATURE ON THE SOLUBILITY IN ALKALI OF A HYDROCELLULOSE, FLUIDITY 32.4 (COPPER NUMBER ABOUT 2.2) (DAVIDSON[26]).

On boiling in alkaline solutions, hydrocellulose exhibits a considerable loss in weight (proportional to the original copper number), a decrease in copper number, only a slight increase in the fluidity, and an increase in solubility in alkaline solutions at low temperatures (see Fig. 16). The increase in low-temperature solubility indicates the formation of short-chain molecules, whereas the relatively small increase in fluidity would indicate little effect on average chain length. The shortening of the cellulose chains would tend to increase the fluidity, but the removal of the shortest as

soluble products would tend to lower it. It appears that the two effects counterbalance one another in such a way that neither the average chain length nor the low-temperature solubility is greatly affected in spite of the considerable losses in weight that occur during the hot alkali treatment.

With the exception of potassium hydroxide, the solubility of acid-modified celluloses in other alkalies is qualitatively similar to its behavior

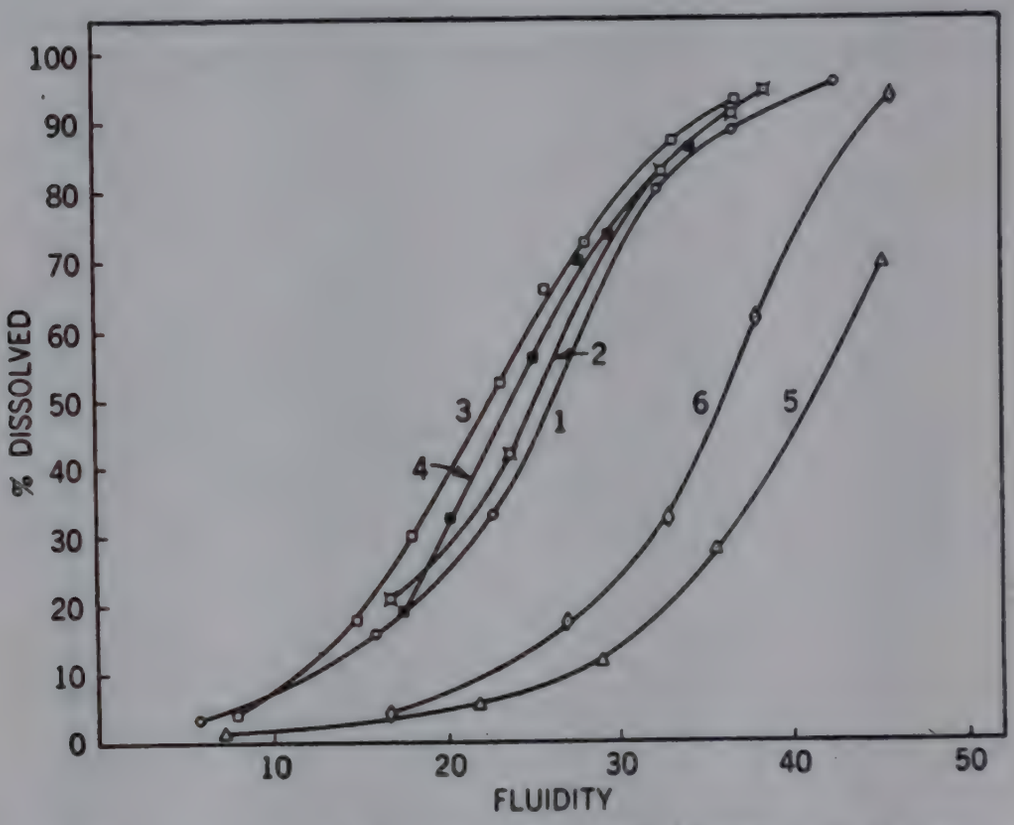

FIG. 16.—THE EFFECT OF AN ALKALI BOIL (2% NaOH FOR 4 HRS. AT EXCESS PRESSURE OF 30 LBS. PER SQ. IN.) ON THE LOW-TEMPERATURE SOLUBILITY (IN 2.5 TO 3.0 *N* NaOH AT −5°C.) AND FLUIDITY OF HYDROCELLULOSE FROM MERCERIZED AND UNMERCERIZED COTTON (DAVIDSON[28]).

Curves 2 and 4 represent cotton samples 1 and 3 after the boil.
Curve 5 represents mercerized cotton.
Curve 6 represents mercerized cotton after boiling.

in sodium hydroxide solutions.[27] The solvent action of potassium hydroxide is small and does not show the temperature sensitivity of sodium hydroxide as demonstrated above.

Cellulose can be made to show a considerable variation in affinity for basic dyes by pretreatment with mineral acids. When cotton is steeped in sulfuric acid, an initial decrease in methylene blue absorption with increase in acid concentration occurs[6]; however, above an acid concentration of 400 g. per liter, the dye absorption is again increased. With phosphoric

acid, a proportionality exists between the phosphoric acid content and methylene blue absorption of the fibers. Early explanations[28] of the increased absorption of the dye by acid-treated celluloses were based on the formation of an adsorption compound of peptized cellulose with the dye. Subsequent work,[29] however, has shown that the increase in methylene blue absorption is proportional to the combined acid content of the cellulose and has offered a more probable explanation for the phenomena. Thus, it is entirely conceivable that the combined sulfuric acid is in the form of a half-ester, leaving a free acidic group which could combine with the basic dye.

[28] W. Harrison, *J. Soc. Dyers Colourists*, **28**, 238 (1912).
[29] D. A. Clibbens and A. Geake, *J. Textile Inst.*, **18**, T168 (1927).

3. Oxycellulose

HENRY A. RUTHERFORD AND MILTON HARRIS

The modifications that cellulose can undergo in oxidizing media are numerous, and accordingly the properties of the reaction products vary widely depending upon the method and extent of oxidative modification. Many of the early investigators did not follow any particular method of preparation of oxycellulose and, as in the case of the hydrocelluloses, much confusion as to the properties of oxycellulose exists in early literature. For this reason, and also because an excellent summary of the work up to 1922 has been presented by Clifford and Fargher,[1] a discussion of most of the early work is not included here.

From a technical point of view, the oxidation of cellulose is a subject of great importance. In the commercial processing of cellulose, for example, bleaching treatments are frequently required to remove the colored substances which impart a yellowish tint to the material; in such treatments, oxidizing agents such as hypochlorite or hydrogen peroxide may be employed, and unless care and control are exercised, severe tendering of the cotton cellulose, due to oxidative degradation, may occur. Cellulose is also readily degraded by oxygen in strongly alkaline solutions,[2] a reaction which is utilized in the preparation of regenerated cellulosic fibers.

[1] P. H. Clifford and R. G. Fargher, *J. Textile Inst.*, **13**, T189 (1922).
[2] G. F. Davidson, *J. Textile Inst.*, **23**, T95 (1932).

(a) *Factors Influencing the Formation of Oxycelluloses*

The properties of any oxycellulose depend upon the method by which it is prepared, but in general it may be said that in neutral or acidic solutions, oxycelluloses of the *reducing* type are formed (*i. e.*, they show a high content

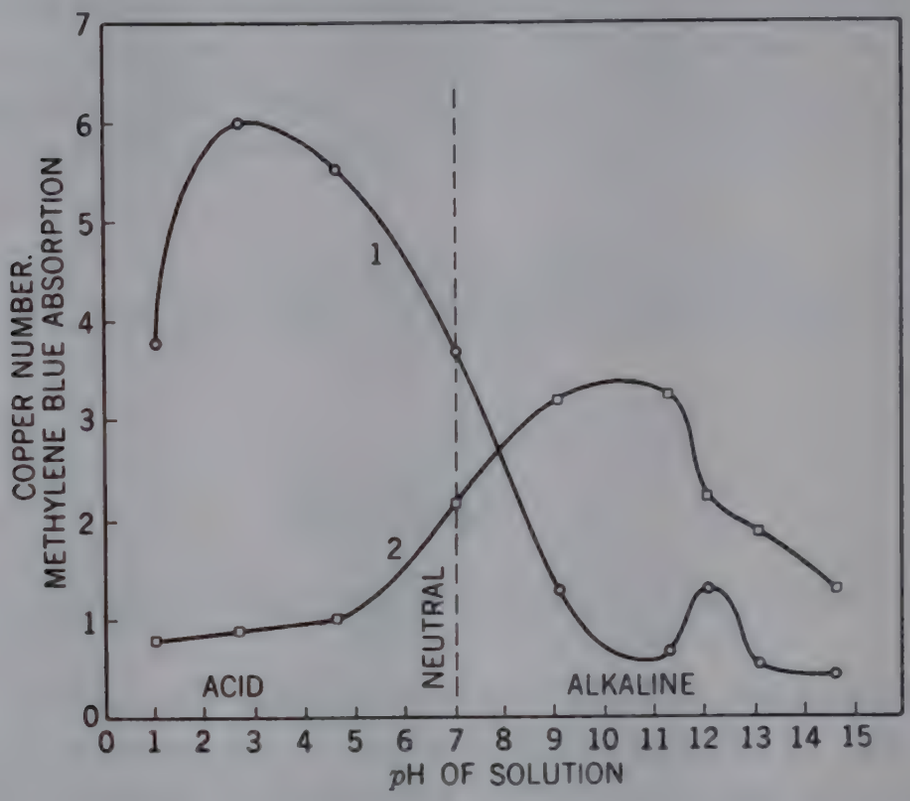

FIG. 17.—INFLUENCE OF HYDROGEN-ION CONCENTRATION OF THE OXIDIZING AGENT ON THE FORMATION OF REDUCING AND ACIDIC GROUPS IN CELLULOSE (BIRTWELL CLIBBENS, AND RIDGE[3]).

Curve 1. Copper number.
Curve 2. Methylene blue absorption.

of reducing groups as measured by the copper number method), whereas in alkaline solutions, the *acidic* type of oxycellulose is formed. The latter has sometimes been referred to as the "methylene blue" type since it exhibits rather high affinity for methylene blue. Acidic oxycelluloses tend to show high retention of alkali presumably due to the presence of carboxylic acid groups.[3, 4, 5]

The manner in which hydrogen-ion concentration may influence the type of oxycellulose obtained is shown in Figure 17. The rate of oxycellulose

[3] C. Birtwell, D. A. Clibbens, and B. P. Ridge, *J. Textile Inst.*, **16**, T13 (1925).
[4] G. F. Davidson, *J. Textile Inst.*, **32**, T132 (1941).
[5] H. A. Rutherford, F. W. Minor, A. R. Martin, and M. Harris, in preparation for publication.

ormation is considerably influenced by *p*H, the most rapid reaction for nost oxidants occurring at or near the neutral point, as indicated by the lata in Figures 18, 19, and 20. The data emphasize the fact that the rate or xtent of oxidation is not necessarily ascertained by the measurement of the

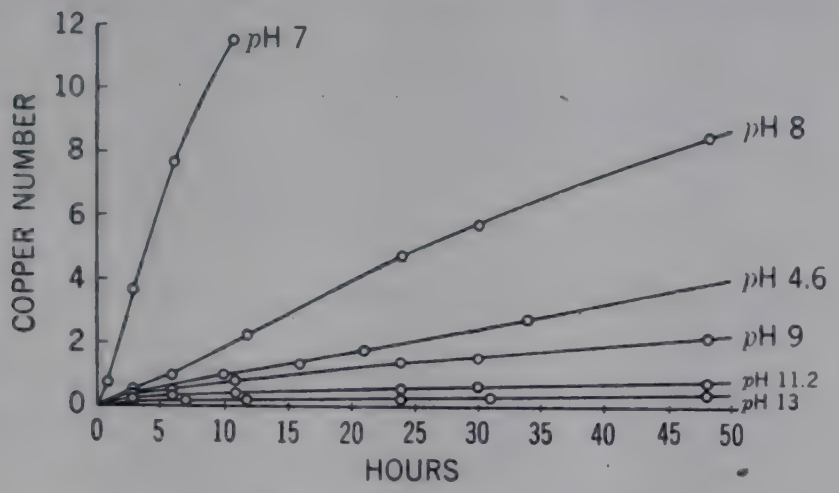

FIG. 18.—THE EFFECT OF *p*H ON THE RATE OF INCREASE OF COPPER NUMBER (CLIBBENS AND RIDGE[6]).

0.04 *N* sodium hypochlorite at 25°C.; ratio of cotton to solution, 1:100.

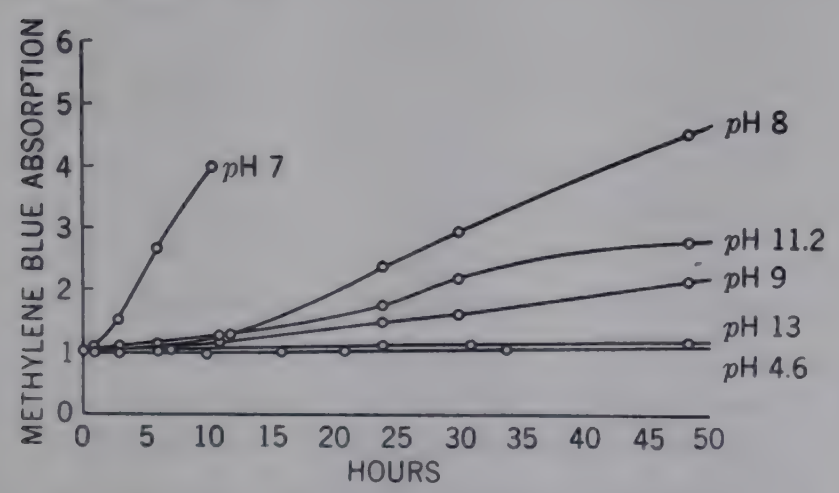

FIG. 19.—THE EFFECT OF *p*H ON THE RATE OF INCREASE OF METHYLENE BLUE ABSORPTION (CLIBBENS AND RIDGE[6]).

0.04 *N* sodium hypochlorite at 25°C.; ratio of cotton to solution, 1:100.

change in any one given property such as copper number or methylene blue absorption; thus, as indicated by the copper number method, the rate is greater at *p*H 4.6 than at *p*H 11.2, whereas, as indicated by methylene blue absorption, the effects of *p*H appear to be reversed.

[6] D. A. Clibbens and B. P. Ridge, *J. Textile Inst.*, **18**, T135 (1927).

The rate of oxycellulose formation is also influenced by temperature, concentration of oxidant, and the nature of the oxidizing reagent itself. As an example of the last, hypobromite is much more effective for a given set of conditions than hypochlorite.[6] Finally the rate of oxidation of the cellulose may be greatly accelerated by the simultaneous oxidation of a third

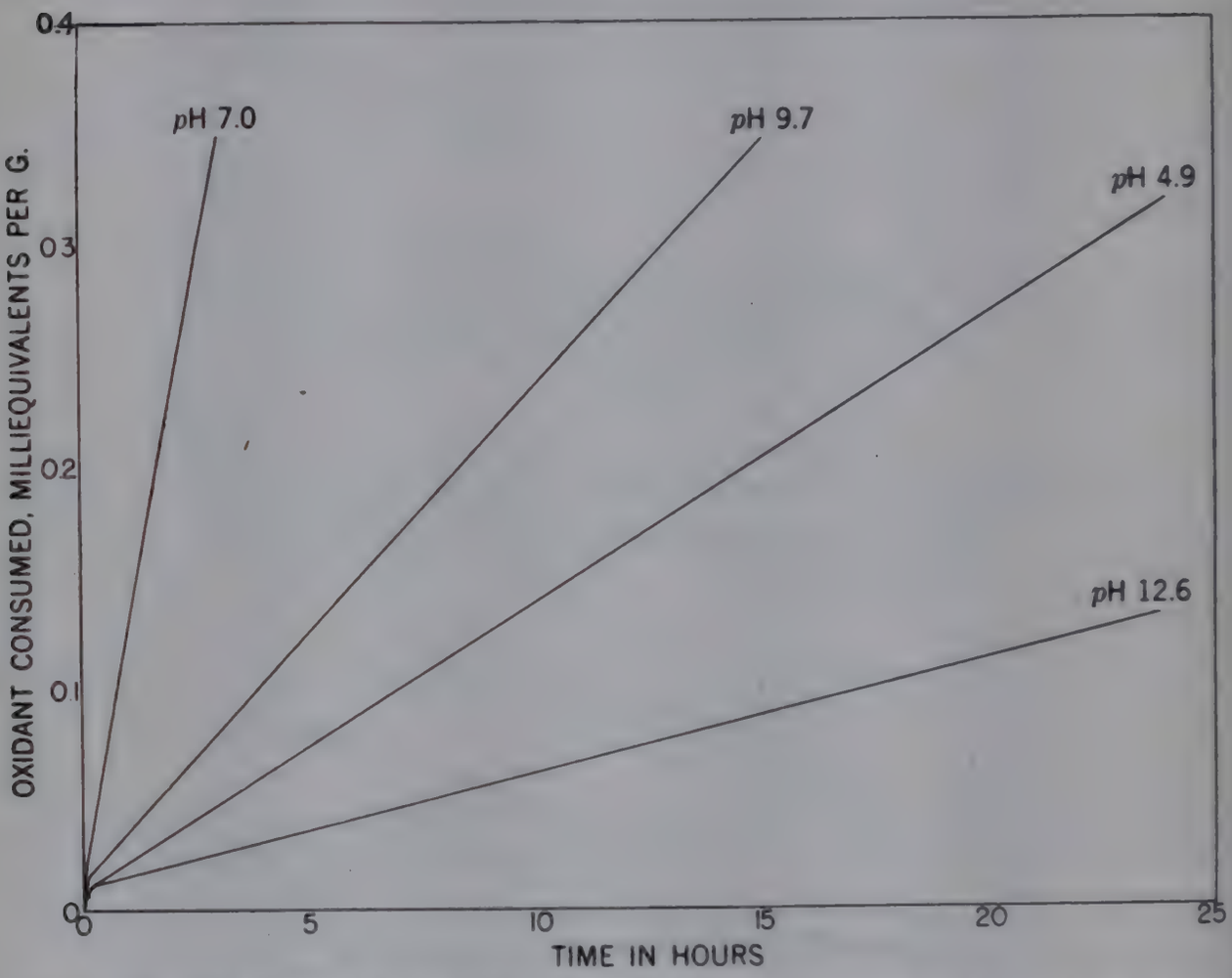

FIG. 20.—THE EFFECT OF *p*H ON THE RATE OF CONSUMPTION OF ACTIVE CHLORINE (RUTHERFORD, MINOR, MARTIN, AND HARRIS[5]).

Conditions: 3 g. per liter of available chlorine; 25°C.; ratio of cotton to solution, 1:100.

substance in the system. Thus, oxidation with dichromate in the presence of oxalic acid is far more rapid than in the presence of sulfuric acid.[6] As another example, it has been shown that when cotton, on which a reduced vat dye has been absorbed, is treated with hypochlorite, the oxidation of the cellulose is greatly accelerated.[7, 8] The method of oxidation with dichromate in the presence of oxalic acid has been suggested as a very con

[7] H. A. Turner, G. M. Nabar, and F. Sholefield, *J. Soc. Dyers Colourists*, **51**, 5 (1935)
[8] G. M. Nabar, F. Sholefield, and H. A. Turner, *J. Soc. Dyers Colourists*, **53**, 5 (1937)

venient one for the preparation of an oxycellulose of the extreme reducing type.

While many oxidizing agents tend to follow this same general trend in respect to *p*H, potassium permanganate is outstandingly different. The maximum rate of oxidation of cellulose by this substance occurs at *p*H 11.2 and the minimum at *p*H 9, the latter value being one at which a marked transition in the nature of the oxidized cellulose occurs.[9] In contrast with hypochlorite, little change in the type of oxycellulose formed with this reagent occurs between *p*H 5 and 9.

(*b*) *Nature of Reactions of Cellulose with Different Oxidizing Agents*

The extensive literature on oxycellulose is indicative of the enormous amount of work which has been done in this field and yet, at the present time, it must be concluded that the chemical mechanism of oxidative attack by most reagents is not clearly understood. It would appear that the attack on cellulose by oxidizing reagents would be confined to three points in the anhydroglucose residue of the cellulose chain: (1) The aldehydic end groups of which there are few if any in native cellulose[10] could be oxidized to carboxyl groups. Such a process would not be expected to result in significant changes in the properties of celluloses of high average chain lengths but might alter considerably the properties of an appreciably degraded hydrocellulose. (2) The primary alcohol groups could be oxidized to the aldehyde or carboxylic acid depending upon the oxidizing conditions. Such oxidations would lead to a reducing type or an acidic type of oxycellulose depending upon whether the reaction proceeded to the aldehyde or to the acid. (3) The glycol group (the 2,3-dihydroxy group) of the glucose residue could be oxidized with the formation of ketonic, aldehydic, or carboxylic groups depending upon the course of the reaction.

A major difficulty in most attempts to ascertain the course of the oxidation of cellulose has been the lack of analytical methods of sufficient specificity and sensitivity to determine accurately the number of any of the above-mentioned groups which might be formed or to allocate them to their positions in the glucose residues. The limitations of such methods as those involving the measurement of copper number as an estimate of reducing groups or methylene blue absorption as an estimate of acidic groups are well recognized and quantitative conclusions based on their use may be

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[9] C. Dorée and A. C. Healey, *J. Soc. Dyers Colourists*, **49**, 290 (1933).

[10] A. M. Sookne and M. Harris, *J. Research Natl. Bur. Standards*, **26**, 205 (1941); *Am. Dyestuff Reptr.*, **30**, 107 (1941).

open to criticism. Nevertheless, considerable use has been made of them and they have been helpful in obtaining a rough qualitative picture of the course of some of the reactions. More recently a number of new methods for the estimation of aldehydic and carboxylic groups in cellulose have been developed[5, 10, 11, 12] and are at present being applied to quantitative studies of the functional groups in various types of oxycelluloses.[5]

Until recently it was widely assumed that the oxidative attack occurred at the primary alcohol groups in the cellulose chain molecules causing either weakening or actual scission of the glucosidic linkages. In favor of this assumption was the fact that many of the oxycelluloses yielded carbon dioxide during boiling with hydrochloric acid, a reaction which is characteristic of uronic acids. Oxidation of the primary alcohol group to the carboxyl group stage would result in the formation of a glucuronic acid anhydride residue.[13, 14, 15]

Unfortunately, the hypothesis of simple oxidation of the primary alcohol group to a carboxylic acid group does not adequately explain the behaviors of all of the various types of oxycelluloses. Thus, Clibbens and Ridge[16] have shown that, whereas there is a proportional increase in cuprammonium fluidity and in copper number with decrease in tensile strength for hydrocelluloses, regardless of the type of acid used in their preparation, this proportionality does not exist for all types of oxycellulose. The data[16] in Table 1 illustrate this point. Similarly, no relationship exists between copper number and tensile strengths for all types of oxycellulose. For example, a rise of one unit in copper number may correspond to complete loss in strength as in the case of alkaline hypochlorite modification, to 50% loss as in tendering by acids, or to practically no loss in strength as in the oxidation with dichromate. Since, on the basis of the molecular chain theory, both the fluidity and the tensile strength of cellulose are regarded as functions of chain length, this apparent anomaly was at first disturbing.

As a solution of this difficulty, Davidson[17, 18, 19] suggested that some types

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[11] A. M. Sookne, C. H. Fugitt, and J. Steinhardt, *J. Research Natl. Bur. Standards*, **25**, 61 (1940).

[12] A. R. Martin, L. Smith, R. L. Whistler, and M. Harris, *J. Research Natl. Bur. Standards*, **27**, 449 (1941); *Am. Dyestuff Reptr.*, **30**, 628 (1941).

[13] E. Heuser and F. Stöckigt, *Cellulosechem.*, **3**, 61 (1922).

[14] L. Kalb and F. Falkenhausen, *Ber.*, **60B**, 2514 (1927).

[15] G. L. Godman, W. N. Haworth, and S. Peat, *J. Chem. Soc.*, **1939**, 1908.

[16] D. A. Clibbens and B. P. Ridge, *J. Textile Inst.*, **19**, T389 (1928).

[17] G. F. Davidson, *J. Textile Inst.*, **29**, T195 (1938).

[18] G. F. Davidson, *J. Textile Inst.*, **25**, T174 (1934).

[19] G. F. Davidson, *J. Textile Inst.*, **27**, P144 (1936).

of oxidation do not result in direct scission of the chain molecules but reduce the chemical stability of some of the linkages in the cellulose chain toward alkalies. This suggestion was based on the discovery of Clibbens and Ridge[16] that the changes in fluidity and strength after boiling oxycelluloses in alkaline solutions were such that the fluidity-strength relation was the same for all types of oxycellulose. Types of oxidation which do not rupture the chain would not have an appreciable effect on strength; at the same time, these types of modification result in a material which is labile toward alkali and accordingly the fluidity in cuprammonium solution will be high. This, then, would explain the apparent lack of correlation between strength and fluidity for all types of oxycelluloses.

On the basis of this reasoning, Davidson further postulated that if the fluidity of this type of oxycellulose could be determined without the use of

TABLE 1

RELATION BETWEEN CUPRAMMONIUM FLUIDITY AND STRENGTH OF HYDROCELLULOSE AND DIFFERENT TYPES OF OXYCELLULOSES (CLIBBENS AND RIDGE[16])

Cuprammonium fluidity	Percentage loss of strength (single-thread breaking load)			
	Caused by acid attack	Caused by attack with hypochlorite or hypobromite	Caused by attack with dichromate plus H_2SO_4	Caused by attack with dichromate plus oxalic acid
10	10	7	2	1
20	34	25	11	6
30	58	47	26	16

alkaline solutions, then it would be possible to obtain a true measure of the average length of the molecular chains as they exist in the fiber. Fortunately, it was found possible to do this by first nitrating the celluloses and then determining the fluidity of the derived nitrocelluloses in acetone or butyl acetate solution.[17, 20] By this procedure, it was found that discrepancies between strength and fluidity (*i. e.*, oxycelluloses which exhibit high strength and high cuprammonium fluidity) disappeared. Thus, oxycelluloses of the type characterized by high strengths also showed low nitrocellulose fluidities.

From the foregoing, it is readily seen why the relationship of cuprammonium to nitrocellulose fluidity as found for all types of hydrocelluloses does not exist for all types of oxycelluloses (Fig. 21). If, however, the oxycelluloses are first boiled in alkaline solution, in order to complete the scis-

[20] E. Berl, *Ind. Eng. Chem., Anal. Ed.*, **13**, 322 (1941).

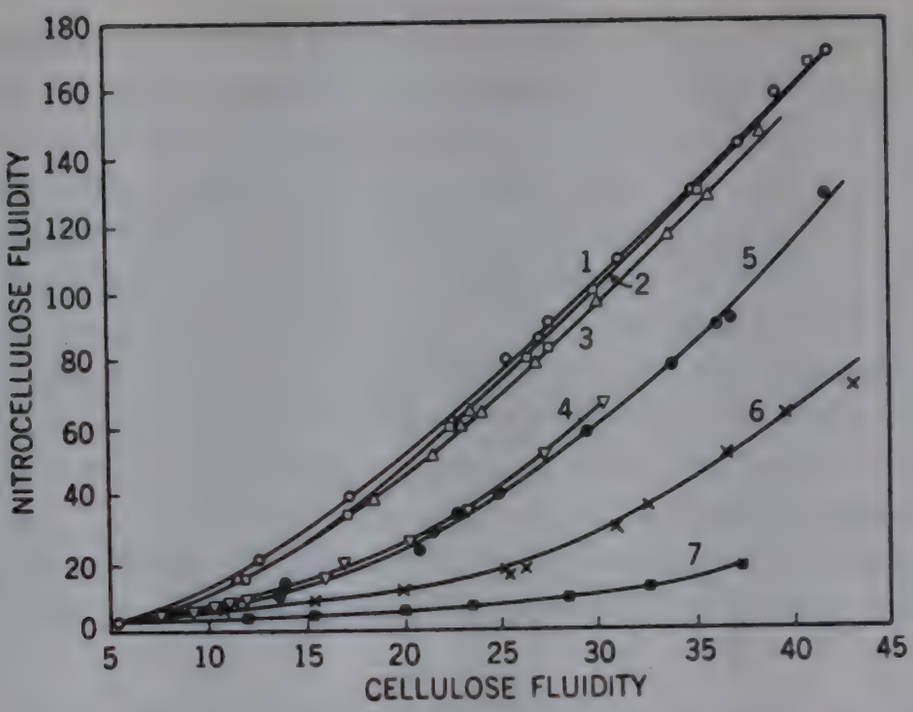


FIG. 21.—RELATION BETWEEN NITROCELLULOSE FLUIDITY AND CUPRAMMONIUM FLUIDITY OF MODIFIED COTTONS (DAVIDSON[17]).

1. Hydrochloric acid.
2. Alkaline hypobromite.
3. Alkaline hypochlorite.
4. Acid hypochlorite.
5. Neutral hypochlorite.
6. Dichromate + sulfuric acid.
7. Dichromate + oxalic acid.

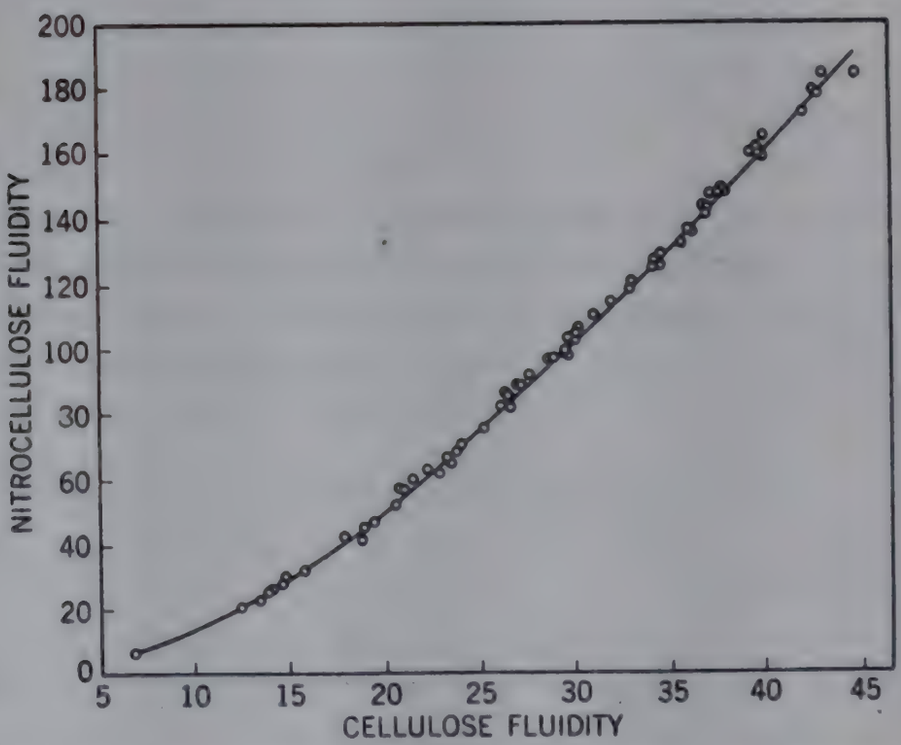
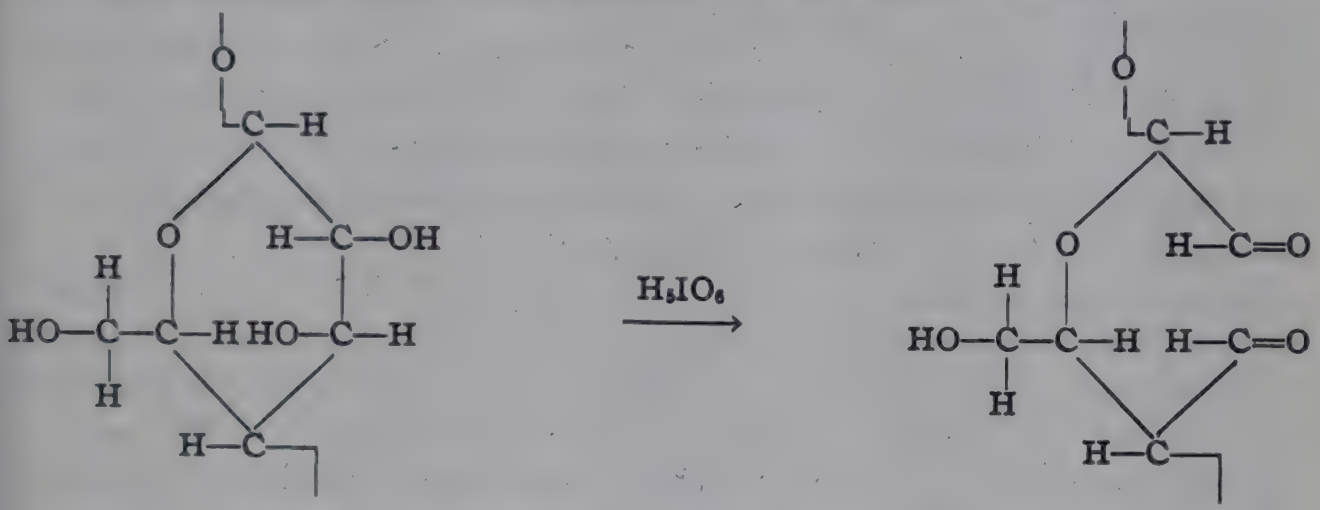


FIG. 22.—RELATION BETWEEN NITROCELLULOSE FLUIDITY AND CUPRAMMONIUM FLUIDITY OF MODIFIED COTTONS AFTER BOILING WITH SODIUM HYDROXIDE SOLUTION (DAVIDSON[17]).

sion of the cellulose chains at the alkali-labile linkages, the nitrocellulose and cuprammonium fluidities change to a greater or less extent depending on the type of oxidative modification, and the relation between the two fluidities can then be expressed by a single curve as shown in Figure 22. These experiments left little doubt that the reducing types of oxycellulose do contain alkali-sensitive linkages.

Davidson's hypothesis received considerable support from the investigations of Jackson and Hudson[21] who showed that in the oxidation of cellulose by periodic acid, cleavage of the glucose ring of the cellulose chain between carbon atoms 2 and 3 occurred with the conversion of the secondary alcoholic groups to aldehydes, according to the following scheme:



Subsequent to the work of Jackson and Hudson, the oxidation of cellulose by periodic acid and metaperiodate has been studied by Davidson extensively,[22, 23] and more recently by Rutherford, Minor, Martin, and Harris.[23a]

It should be emphasized that the oxidation of cellulose with other oxidizing agents does not necessarily follow the mechanism suggested by periodic acid studies. The reactions of cellulose with such oxidizing agents as hypochlorite, hypobromite, and dichromate, appear to be more complex. In fact, certain properties of celluloses modified by these agents make it clear that the mechanism does not follow that of periodic acid.[4, 23] In addition, oxycelluloses, which on the basis of certain criteria are of the same type, have been found to yield products which vary considerably in other

[21] E. L. Jackson and C. S. Hudson, *J. Am. Chem. Soc.*, **58**, 378 (1936); **59**, 994, 2049 (1937); **60**, 989 (1938).

[22] G. F. Davidson, *J. Textile Inst.*, **31**, T81 (1940).

[23] G. F. Davidson, *J. Textile Inst.*, **32**, T109 (1941).

[23a] H. A. Rutherford, F. W. Minor, A. R. Martin, and M. Harris, *J. Research Natl. Bur. Standards*, **29**, 131 (1942); *Am. Dyestuff Reptr.*, **31**, 399 (1942).

properties. Thus, Davidson[4, 23] has recently compared the properties of oxycellulose prepared with chromic acid and periodic acid and has observed rather profound differences in their behavior, although both reagents give reducing oxycelluloses as determined by the copper number method. He suggests that the cellulose is more uniformly attacked by the latter reagent, whereas the action of chromic acid is limited primarily to the noncrystalline regions. Supporting this suggestion is the fact that the x-ray patterns are not destroyed by a high degree of oxidation with chromic acid, whereas periodate gradually destroys the characteristic x-ray diagram of cellulose.

A different explanation for the behavior of chromic acid toward cellulose has been put forth by Staudinger and Sohn[24] who suggest that glucosidic linkages are converted to carbonic ester linkages, such linkages accounting for the alkali-lability of oxycellulose. However, as already pointed out by Davidson, a similar reason could be given to explain the mechanism of oxidation by periodic acid, which produced oxycelluloses that are even more alkali-labile than chromic acid oxycelluloses.

Another mechanism of oxycellulose formation which has been advanced involves as a primary reaction the splitting of 1,4-glucosidic linkages.[25] This cannot be considered to be a general reaction since oxidations can occur under conditions which do not produce significant changes in chain length.

A very different type of oxidation has recently been described by Kenyon and his coworkers[26, 27] who used nitrogen dioxide as the oxidizing agent. In contrast with most types of oxidations, which when carried to excess result in complete disintegration of cellulose fibers, it was found that at any stage of oxidation with nitrogen dioxide, the cellulose still retains its fibrous structure. Of especial interest, however, is the fact that the oxidation appears to be confined entirely to the primary alcoholic groups and results in the conversion of these groups to carboxylic acid groups. Oxycelluloses having carboxyl contents which approached theoretical values calculated on the assumption that all primary alcoholic groups have been oxidized were prepared by these investigators.

The effects of another gaseous oxidizing agent, ozone, have been investigated.[28] It was found that, in the presence of water, the reducing type of

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[24] H. Staudinger and A. W. Sohn, *Ber.*, **72B**, 1709 (1939); *Melliand Textilber.*, **21**, 205 (1940).

[25] S. M. Kaji and K. Venkataraman, *Current Sci.*, **9**, 66 (1940).

[26] E. C. Yackel and W. O. Kenyon, *J. Am. Chem. Soc.*, **64**, 121 (1942).

[27] C. C. Unruh and W. O. Kenyon, *J. Am. Chem. Soc.*, **64**, 127 (1942).

[28] C. Dorée and A. C. Healey, *J. Textile Inst.*, **29**, T27 (1938).

oxycellulose is the principal product although a slight increase in methylene blue absorption occurs. This is attributed, as in the case of other oxidizing substances, to the formation of some carboxyl groups. The rate of oxycellulose formation by ozone is greatly inhibited by first acetylating the cellulose, while the effect of mercerization is the reverse; that is, oxycellulose formation is accelerated by pretreatment with alkali.

A number of oxidizing agents such as hydrogen peroxide[29] and sodium chlorite appear to be much less drastic in their effect on cellulose and accordingly have found use in commercial bleaching processes. It has been claimed that the latter bleaches cotton goods without affecting oxycellulose formation.[30]

Finally, it should again be pointed out that, while the oxidation of cellulose by periodic acid is confined largely to the glycol group and that produced by nitrogen dioxide to the primary hydroxyl group of the glucose residue, other oxidizing agents are less specific and probably result in mixtures of the above reactions. This fact has seriously complicated attempts to elucidate the nature of the chemical reactions involved. Further advances in our understanding of the nature of the reactions of various oxidizing agents with cellulose will depend on a more accurate evaluation of the number, type, and location of the ketonic, aldehydic, or carboxylic acid groups which may be produced during oxycellulose formation. The recent development of a number of useful techniques, some of which are described in Section C of this chapter, should prove very helpful.

(*c*) *Properties of Oxycelluloses*

One of the most striking characteristics of oxycelluloses is the change in properties that takes place when these materials are treated with alkaline solutions. The reducing value (copper number) is so diminished under certain conditions that the remaining cellulose cannot be distinguished in this respect from unmodified cellulose. Some of the reducing power lost by the oxycellulose is gained by the extract[15, 31] and this may or may not be accompanied by appreciable weight losses depending upon the type of oxycellulose in question. The effect of an alkali boil on oxycelluloses of the various types is shown in Table 2.[32] The reducing power of the oxy-

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[29] H. Staudinger and J. Jurisch, *Papier-Fabr.*, **35**, Tech.-wiss. Tl., 463 (1937).

[30] G. P. Vincent, A. L. Dubeau, and J. F. Synan, *Am. Dyestuff Reptr.*, **30**, 358 (1941).

[31] C. Birtwell, D. A. Clibbens, and A. Geake, *J. Textile Inst.*, **19**, T349 (1928).

[32] Compiled from data in J. T. Marsh and F. C. Wood, *An Introduction to the Chemistry of Cellulose.* Chapman & Hall, London, 1938.

TABLE 2

EFFECT OF ALKALI BOIL ON THE COPPER NUMBER AND METHYLENE BLUE ABSORPTION OF OXYCELLULOSES (MARSH AND WOOD[32])

Type of oxycellulose	Copper number		Methylene blue absorption	
	Before alkali boil	After alkali boil	Before alkali boil	After alkali boil
Acid hypochlorite	0.65	0.09	1.02	0.90
	1.07	0.17	1.04	1.02
	2.46	0.39	1.10	1.21
Neutral hypochlorite	1.02	0.22	0.96	..
	2.02	0.47	1.01	1.18
	3.22	0.66	1.36	1.66
Alkaline hypochlorite	0.02	0.02	1.08	0.95
	0.35	0.02	1.56	1.30
	0.50	0.09	2.95	2.45

TABLE 3

EFFECT OF VARIOUS TREATMENTS ON THE CUPRAMMONIUM FLUIDITY (F_C) AND NITROCELLULOSE FLUIDITY (F_N) OF MODIFIED COTTONS (DAVIDSON[17, 22])

Treatment	Hydrochloric acid		Alkaline hypobromite		Alkaline hypochlorite		Neutral hypochlorite	
	F_C	F_N	F_C	F_N	F_C	F_N	F_C	F_N
Original modified cotton	27.6	90.9	29.8	100.4	29.9	96.6	29.5	58.6
Water, 100°C., 6 hrs.	27.6	91.6	31.2	106.6	30.7	103.8	34.5	116.4
Soap, 1%, 100°C., 6 hrs.	27.6	93.8	31.4	109.4	30.0	102.9	35.6	128.9
Na_2CO_3, 1%, 100°C., 6 hrs.	27.9	94.6	32.0	115.0	30.9	106.0	35.5	132.5
NaOH, 1%, 126°C.,* 6 hrs.	28.7	96.8	34.2	127.4	33.1	120.7	36.0	136.9
NaOH, 0.5 *N*, 20°C., 24 hrs.	27.3	90.3	30.5	109.8	29.6	102.2	35.3	121.9
NH_4OH, 200 g./l., 20°C., 24 hrs.	27.6	92.3	..	...	30.4	99.9	31.1	84.7

Treatment	Acid hypochlorite		Dichromate plus H_2SO_4		Dichromate plus oxalic acid		Periodic acid	
	F_C	F_N	F_C	F_N	F_C	F_N	F_C	F_N
Original modified cotton	30.2	67.5	31.0	30.5	28.4	10.1	29.2	5.2
Water, 100°C., 6 hrs.	37.5	132.4	32.4	81.4	29.5	69.3	30.1	37.7
Soap, 1%, 100°C., 6 hrs.	42.0	168.5	34.5	115.1	29.2	85.7	27.5	87.5
Na_2CO_3, 1%, 100°C., 6 hrs.	41.9	169.4	34.5	125.1	28.6	96.0	27.3	89.5
NaOH, 1%, 126°C.,* 6 hrs.	42.0	171.3	34.6	129.5	30.2	104.6	27.7	92.9
NaOH, 0.5 *N*, 20°C., 24 hrs.	41.0	161.1	34.1	108.6	29.5	76.7	27.5	81.6†
NH_4OH, 200 g./l., 20°C., 24 hrs.	33.7	110.5	31.8	62.1	29.7	38.8	29.0	71.4

* 20 lb./sq. in. excess pressure.

† 0.1 *N* NaOH, 20°C., 24 hrs.

cellulose decreases to a small value while the methylene blue absorption is virtually unaffected by the treatment.

Another marked change that occurs on alkaline treatment is the increase in fluidity of the derived nitrocelluloses (see Figs. 21 and 22). Because of the sensitivity of the fluidity determination, it is possible to detect small changes in average chain length of oxycelluloses produced by treatment with reagents which are less drastic than boiling sodium hydroxide solutions. Thus, even boiling water degrades reducing types of oxycellulose. An even more striking confirmation of the hypothesis of alkali-sensitive linkages in reducing oxycelluloses is afforded by the effect of cold (20°C.) solutions of sodium hydroxide on the nitrocellulose fluidity. Under these conditions the modified cellulose does not suffer any apparent profound change or loss in weight as compared with that which occurs in hot alkaline treatments, yet the fluidity of the derived nitrocellulose is greatly increased. The data in Table 3 show the effect of various solutions on a number of oxycelluloses and one hydrocellulose, all of which had about the same initial cuprammonium fluidity.

The efficacy of alkaline solutions in producing further degradation of oxycelluloses is apparently not dependent solely on hydroxyl-ion concentrations.[17] A comparison of the effects on the nitrocellulose fluidity of modified cellulose after treatment with sodium hydroxide and with cuprammonium hydroxide solutions of approximately the same hydroxyl-ion concentration, showed that the former had a greater effect on an acid hypochlorite oxycellulose while the latter had a greater effect on other types, such as dichromate-oxalic acid oxycelluloses. The effects of other basic compounds, such as Triton F (dibenzyldimethylammonium hydroxide), Triton B (benzyltrimethylammonium hydroxide), and cupri-ethylenediamine (all of which have been used for fluidity determinations), on the fluidity characteristics of modified celluloses have also been investigated.[33] The degrading action of Triton F on alkali-sensitive modified celluloses appears to be similar to that of the inorganic alkalies. The fluidity in this solvent, unlike that in cuprammonium, is said to be a measure of the total chemical deterioration of the cellulose; that is, the solvent completely ruptures all alkali-labile linkages.

The solubility of oxycelluloses in alkaline solutions has been extensively investigated.[18, 33, 34] In general, the maximum solubility of the oxycellu-

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[33] T. Brownsett and G. F. Davidson, *Shirley Inst. Mem.*, **17**, 127 (1939–40); T. Brownsett and D. A. Clibbens, *Shirley Inst. Mem.*, **17**, 134, 147 (1939–40).

[34] G. F. Davidson, *J. Textile Inst.*, **27**, T112 (1936).

lose occurs at an alkali concentration of about 2.5 *N* and, like hydrocellulose, is considerably more soluble at low temperatures. Again, as found for hydrocellulose, potassium hydroxide shows the least solvent action of those bases studied. At 15°C. the order of increasing solvent action is LiOH < NaOH < $(CH_3)_4NOH$, while at −5°C. the order changes to $(CH_3)_4NOH$ < LiOH < NaOH. Pretreatment of oxycellulose with hot

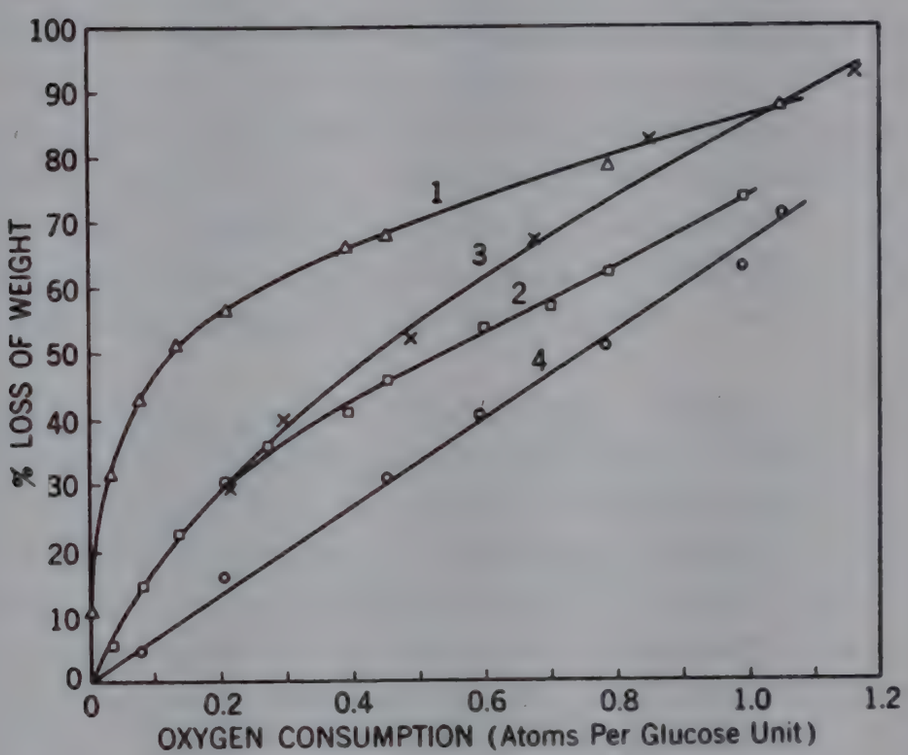

FIG. 23.—LOSS OF WEIGHT BY PERIODIC ACID OXYCELLULOSES ON TREATMENT WITH DILUTE ALKALI AND HOT WATER (DAVIDSON[22]).

	Oxidant	*Treatment*
1.	Periodic acid	0.25 *N* NaOH, 100°C., 6 hrs.
2.	Periodic acid	0.1 *N* NaOH, 20°C., 24 hrs.
3.	Metaperiodate	0.1 *N* NaOH, 20°C., 24 hrs.
4.	Periodic acid	Water, 100°C., 6 hrs.

dilute alkali under pressure results in a residual material more soluble in sodium hydroxide at −5°C. than the original modified cellulose.

It is interesting to note that the differences in the reducing types of oxy-

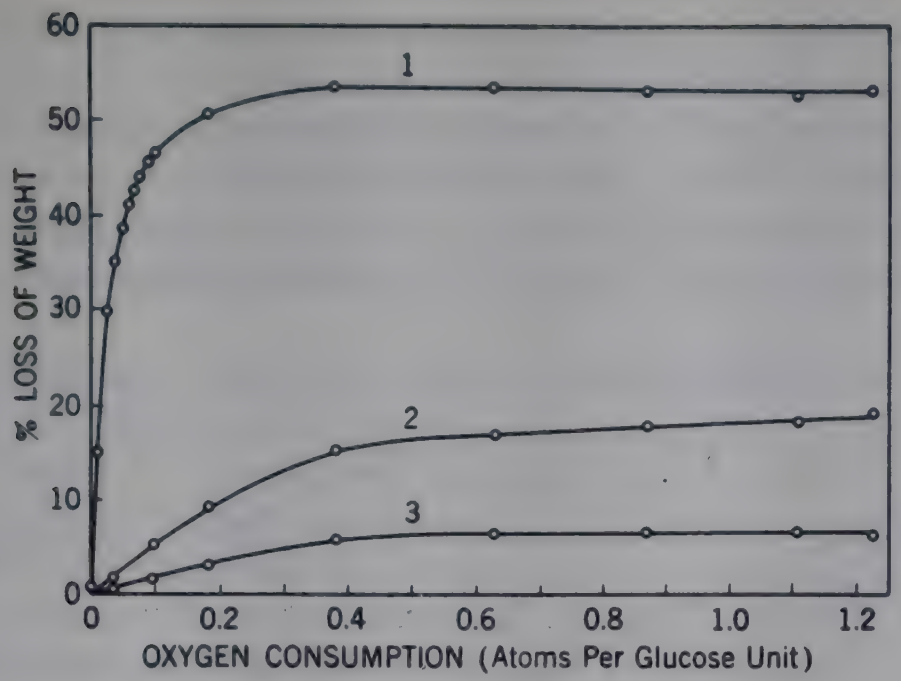

FIG. 24.—LOSS OF WEIGHT BY CHROMIC ACID OXYCELLULOSES ON TREATMENT WITH DILUTE ALKALI AND HOT WATER (DAVIDSON[4]).

1. 0.25 *N* NaOH, 100°C., 6 hrs.
2. 0.1 *N* NaOH, 20°C., 24 hrs.
3. Water, 100°C., 6 hrs.

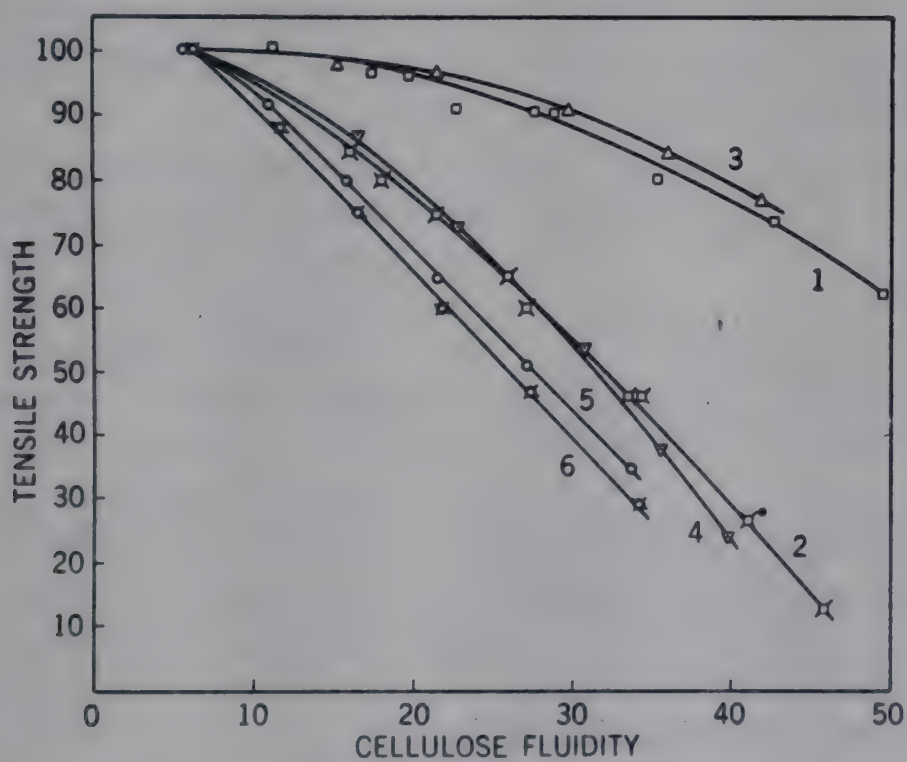

FIG. 25.—RELATION BETWEEN TENSILE STRENGTH AND CUPRAMMONIUM FLUIDITY OF MODIFIED COTTON (DAVIDSON[22]).

1. Periodic acid oxycelluloses.
2. Periodic acid oxycelluloses, boiled.
3. Dichromate oxycelluloses.
4. Dichromate oxycelluloses, boiled.
5. Hydrocelluloses.
6. Hydrocelluloses, boiled.

celluloses produced by periodic and chromic acids, which were discussed earlier, are also evident in respect to the solubilities of these materials in sodium hydroxide.[4, 23] Figures 23 and 24 show the loss in weight under given conditions of these types of oxycelluloses. The chromic acid oxycelluloses reach a maximum solubility at an oxygen consumption of about 0.5 atom for each glucose unit; no such maximum is attained with periodic acid oxycelluloses.

Although oxycellulose formation is in many cases accompanied by a decrease in the strength of the fibrous cellulose, the use of strength measurements as a measure of extent of oxidation may be misleading. This follows from the above discussion of the action of specific oxidizing agents in which it was pointed out that reducing oxycelluloses, such as those produced by periodic acid, show little if any loss in strength although an appreciable amount of oxidation has occurred. The relation of strength to cuprammonium fluidity is illustrated in Figures 25 and 26.

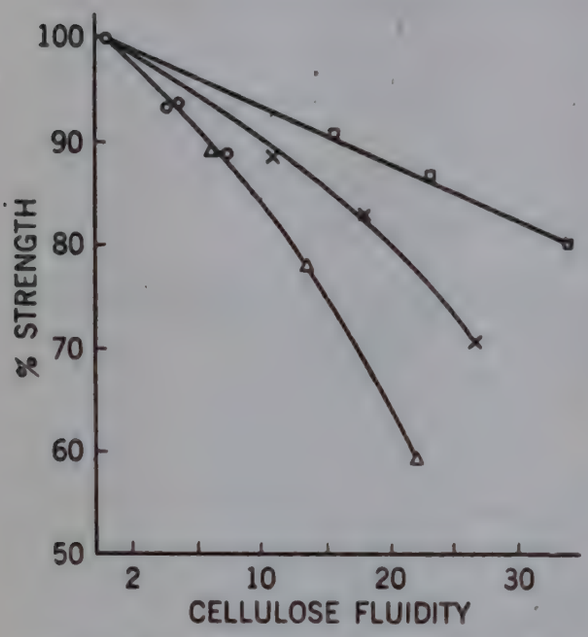

FIG. 26.—RELATION BETWEEN TENSILE STRENGTH AND CUPRAMMONIUM FLUIDITY OF MODIFIED COTTON (DAVIDSON[17]).

Δ—Alkaline hypochlorite.
○—Neutral hypochlorite.
×—Dichromate + sulfuric acid.
□—Dichromate + oxalic acid.

Acidic oxycelluloses, such as those produced by alkaline hypochlorite or by nitrogen dioxide, also vary in properties depending on the oxidizing agents and the conditions of oxidation. Nitrogen dioxide oxycelluloses[26, 27] which have carboxyl contents of 13% and above (theoretical for complete oxidation of primary alcoholic groups = 25.5%) are completely soluble in dilute aqueous solutions of sodium hydroxide, ammonia, sodium carbonate, and pyridine. The soluble salts formed with these bases may be precipitated by alcohol or other water-miscible nonsolvents. With polyvalent ions such as barium, insoluble salts are formed. The copper numbers of these oxycelluloses, which presumably should be low, are indeed very high; a sample which is completely oxidized gives a value which is theoretical for anhydroglucuronic acid calculated on the basis of the reducing power of one aldehyde group for each uronic acid residue. These results, as well as those obtained with incompletely oxidized materials, indicate that the

copper number has no significance in respect to the original oxycelluloses of this type, but rather that reducing groups are formed during degradation in the alkaline copper solutions used in the copper number method. That the carboxyl groups produced in oxidation of cellulose by nitrogen dioxide are of the uronic type is shown by evolution of carbon dioxide when the material is boiled in hydrochloric acid.

TABLE 4

COMPARISON OF THE PROPERTIES OF HYDROCELLULOSES AND OXYCELLULOSES OF THE REDUCING AND ACIDIC TYPES

Qualitative Summary of Data Contained in Refs. 16, 17, 22, 32

Tests	Hydrocellulose	Oxycellulose	
		Reducing	Acidic
Loss in weight on alkali boil	Small	Large	Small
Properties of residue	Same as unmodified cotton. Fluidity approximately same as original hydrocellulose	Same as unmodified cotton except for fluidity	Same as original oxycellulose
Change in nitrocellulose fluidity on alkali boil	Small	Large	Intermediate
Copper number	Intermediate	Large	Small
Methylene blue absorption	Very small	Small	Large
Color with alkali	Very slight yellow	Yellow	No color
Reducing action on $Ag(NH_3)_2OH$	None	Positive	None
Reaction with phenylhydrazine	Positive	Positive	Negative
Hydrazines of biphenyl and naphthalene series	Negative	Positive	Negative
Sn-Au test	Negative	Negative	Positive

(*d*) *Methods of Distinguishing Oxycelluloses from Hydrocelluloses*

The reducing type of oxycellulose may be distinguished from hydrocellulose by the apparent relatively greater reactivity (probably due in part to the greater number) of the aldehydic groups of the oxycellulose. Since such comparative tests are made on an arbitrary basis, it is always necessary to have identical experimental conditions. The Prussian blue reaction and Nessler's test[35] are said to be negative for hydrocellulose while oxycellulose assumes a blue or yellow color. The reduction of silver, copper,

[35] R. Haller, *Z. Textil-Ind.* (*Klepzig's*), **40**, 79 (1937).

iron,[36] and Schiff's reagent is also effected at a greater rate by oxycellulose.

The acidic types are more easily differentiated from hydrocellulose because of the presence of carboxyl groups. These oxycelluloses evolve carbon dioxide with boiling hydrochloric acid and show a high (relative) affinity for metals and basic dyes. The cochineal reaction[35] and the tin-gold (stannous chloride-gold chloride) tests are useful in this respect.[35, 37]

A general comparison of the properties of the various types of modified cellulose of a given cuprammonium fluidity range (10–20) is shown in Table 4.

[36] H. A. Thomas, *J. Soc. Chem. Ind.*, **52**, 79T (1933).
[37] R. Haller, *Melliand Textilber.*, **12**, 257 (1931).

4. Effect of Light, Heat, and Laundering on Cellulosic Materials

Henry A. Rutherford and Milton Harris

In addition to degradation of cellulose by the hydrolytic and oxidative reagents discussed in the foregoing sections, cellulosic materials are also readily degraded by light and heat, and during laundering.

(*a*) *Effect of Light*

The effect of light was noted as early as 1883 when Witz[1] found that cotton which had been exposed to sunlight in the presence of air and moisture showed an increased affinity for methylene blue. During the following forty years a few papers appeared describing the deleterious effects of light, but for the most part the observations were limited to the study of the effects of various wave-lengths and the surrounding atmosphere on the rate of decrease in tensile strength. A summary of the literature over this period has been made by Cunliffe.[2]

The rate of photochemical deterioration of cellulose may depend upon a number of factors. Short-wave ultraviolet rays have been shown to have the most rapid action.[3, 4, 5] In the presence of oxygen,[6, 7] metallic catalysts,[4]

[1] G. Witz, *Bull. soc. ind. Rouen*, **11**, 188 (1883).
[2] P. W. Cunliffe, *J. Textile Inst.*, **14**, T314 (1923).
[3] H. Kauffman, *Melliand Textilber.*, **7**, 617 (1926).
[4] H. J. Henk, *Melliand Textilber.*, **19**, 730 (1938).
[5] S. Uguri and M. Takir, *J. Soc. Chem. Ind., Japan*, **41**, suppl. binding, 3 (1938).
[6] A. C. W. Bot and A. C. van Vreeswijk, *Melliand Textilber.*, **20**, 115 (1939).
[7] V. Sharvin and A. Pakshver, *Z. angew. Chem.*, **41**, 1159 (1928).

or certain dyestuffs,[4, 8] the rate is generally accelerated. The effects of the last, as might be expected, vary with the type of compound. In some cases, however, a protective action has been noted; thus, certain sulfur dyes (excluding those which liberate sulfuric acid on irradiation), vat dyes of the anthraquinone series, and the diazo dyes generally protect the cellulose from oxidation.[4]

Because of the apparent complexity of the reactions and the lack of suitable analytical methods, the effects of light on cellulose have been difficult to evaluate and hence little can be said in respect to the chemical nature of the degradation. The degradation is always accompanied by an increase in fluidity and a loss in strength,[4, 9, 10] and this is taken to indicate a scission in the molecular chain. An increase in reducing power on irradiation, as measured by the copper number method, has also been observed by a number of investigators,[9, 11, 12, 13] but whether these reducing groups arise from hydrolytic or oxidative processes has not yet been established. The liberation of carbon dioxide and water as irradiation products,[7] the formation of reducing groups in the absence of moisture,[11] and the increase in rate of decomposition in the presence of oxygen, however, suggest that the reaction is of the oxidative type.

Not all cellulosic fibers appear to behave similarly when exposed to light, some types being more rapidly degraded than others.[6] Bot and van Vreeswijk[6] have found, for example, that the absorption of oxygen by various fibers upon irradiation increased in the order: cotton, linen, hemp, and jute.

A recent investigation by Launer[12, 13] of the factors influencing the effect of light on paper has yielded interesting results: when light sources of high intensity (including sunlight) were used for comparative studies, it was found necessary to exert careful control of temperature. This is illustrated by the data in the table on the next page.

Experiments conducted, under conditions of carefully controlled temperature and concentrations of water vapor and oxygen, have indicated that the lack of oxygen greatly hinders but does not stop the photochemical deterioration of cellulose. It is interesting to note that water vapor accelerated the effect of light on paper made from cotton cellulose but had

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[8] A. Landolt, *J. Textile Inst.*, **22**, A41 (1931).
[9] S. Uguri, *J. Soc. Chem. Ind., Japan*, **37**, suppl. binding, 201 (1934).
[10] B. dePuyster, *Color Trade J.*, **13**, 23 (1923).
[11] C. W. Mason and F. B. Rosevear, *J. Am. Chem. Soc.*, **61**, 2995 (1939).
[12] H. F. Launer and W. K. Wilson, *J. Research Natl. Bur. Standards*, **30**, 55 (1943).
[13] H. F. Launer, *J. Research Natl. Bur. Standards*, **24**, 567 (1940).

the reverse effect on wood pulp paper. Free rosin and sulfuric acid increased the effect of light upon cotton, rag, and purified wood pulp papers much more than upon inferior papers. The deterioration of the papers was inhibited by the printer's ink but increased by light-absorbing dyes.

DECREASE IN ALPHA-CELLULOSE PERCENTAGE FOR THREE DIFFERENT PAPERS

Sheet temperature at 30°C.	Sheet temperature not controlled
%	%
3.6	54.7
3.8	31.2
1.1	4.5

The use of cellulose derivatives in fibers and plastics is constantly becoming more widespread and it is interesting to note that one of the factors influencing the utility of the latter is their stability to light. For this reason extensive studies of the effect of light on plastics have been made by Kline and his coworkers.[14] The results of their work indicate that the rate at which the various derivatives are degraded is greatly influenced by temperature and moisture.

The photochemical degradation of methylcellulose in dioxane solutions by ultraviolet light has also been investigated.[15, 16] It was noted that the viscosity of the solution decreased, both in the absence or presence of oxygen, a fact which led the authors to conclude that the degradation resulted from true photolysis of the methylcellulose.

(*b*) *Effect of Heat*

The first noticeable result of the effect of heat on cellulose is loss of water. In the temperature range below 140°C., cellulose appears to undergo little change, provided that the initial water content is low and that heating is not prolonged for periods longer than four hours.[17] Above temperatures of 140°C., reducing groups[18, 19] are formed and the fluidity slowly increases.[6, 20, 21] Most regenerated celluloses, under the influence of heat as

[14] G. M. Kline, W. A. Crouse, and B. M. Axilrod, *Modern Plastics*, **17**, 49 (1940).
[15] E. Steurer, *Z. physik. Chem.*, **B47**, 127 (1940).
[16] E. Steurer and H. Mertens, *Ber.*, **74B**, 790 (1941).
[17] C. Dorée, *The Methods of Cellulose Chemistry*. Van Nostrand, New York, 1933.
[18] E. Knecht, *J. Soc. Dyers Colourists*, **36**, 195 (1920).
[19] H. Fletcher and M. Houston, *Textile Research*, **11**, 4 (1940).
[20] H. Staudinger and J. Jurisch, *Papier-Fabr.*, **37**, Tech.-wiss. Tl., 181 (1939).
[21] H. Staudinger and E. Dreher, *Ber.*, **69B**, 1090 (1936)

well as light, show rapid loss in strength, these changes being accompanied by an increase in copper number and alkali solubility of the materials.[19]

In a recent study of effects of drying conditions on the properties of textile yarns,[22] it was shown that the "quality index" (defined as the percent-

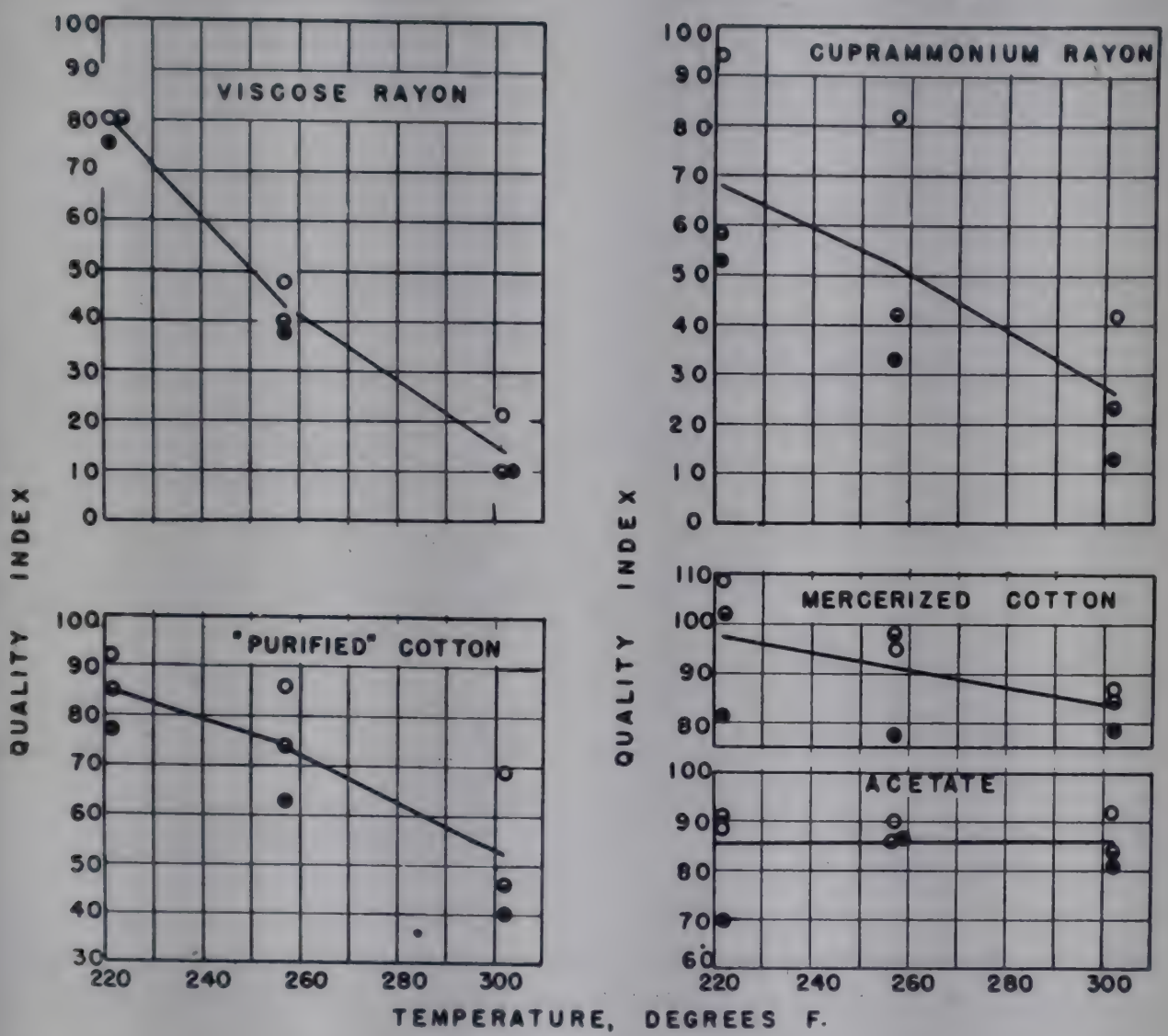

FIG. 27.—EFFECT OF HEAT ON THE "QUALITY INDEX" OF YARNS AT LOW (○), MEDIUM (◒), AND HIGH (●) HUMIDITIES (WIEGERINK[22]).

age of the original breaking strength retained after drying multiplied by the percentage of the original elongation retained after drying) of cellulosic fibers decreases either as the temperature is increased or as the moisture content of the surrounding atmosphere is increased (Fig. 27). The deterioration as measured by the fluidity method is shown in Figure 28, and corresponds well with the quality indices shown in Figure 27. Both the breaking

[22] J. G. Wiegerink, *J. Research Natl. Bur. Standards*, **25**, 435 (1940).

strength and fluidity of the purified cotton and the viscose rayon (Fig. 29) appear to be functions of the relative humidity at which the samples are exposed. However, acetate rayon does not show this sensitivity to moisture. The degradation of cellulose has been shown to be slower in the absence of oxygen which indicates that the initial stages of breakdown, at least, include oxidative destruction.[6, 17] Continued heating, however, in the absence of oxygen leads to deterioration of the cellulose, but little is known of the course of the reactions. If the cellulose is exposed to rela-

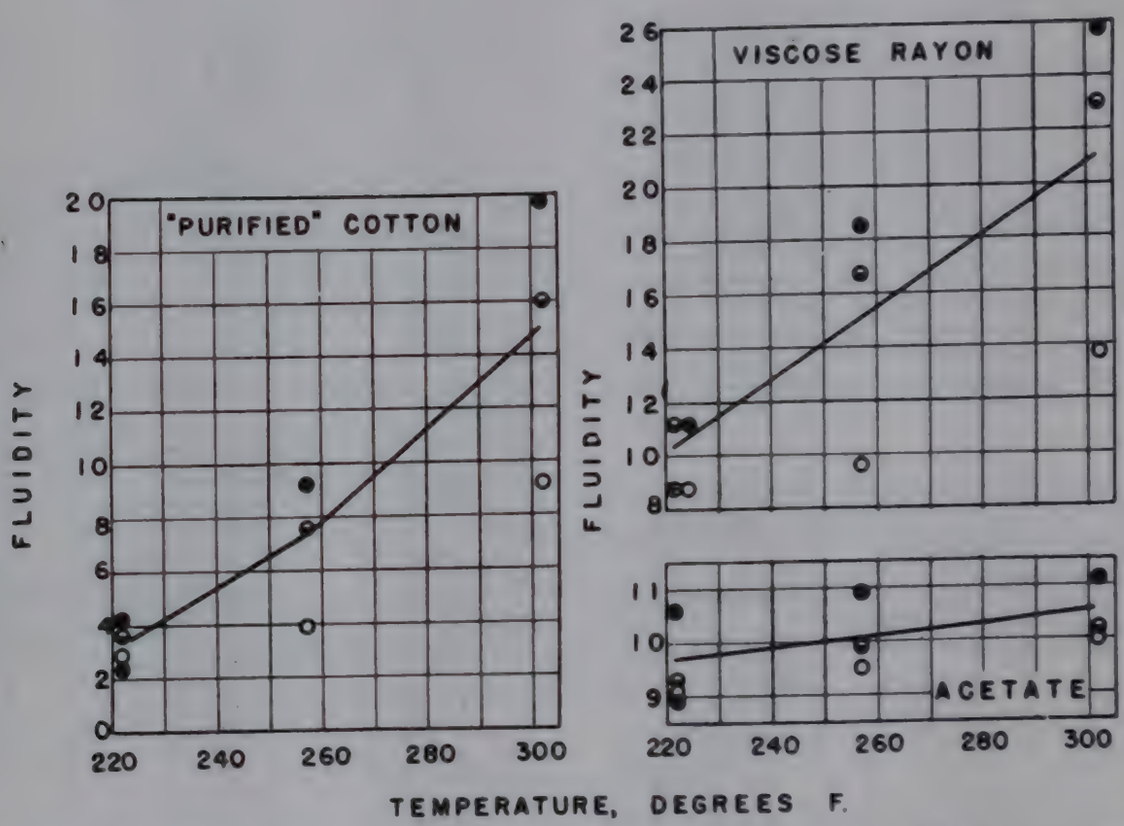

FIG. 28.—EFFECT OF HEAT ON THE FLUIDITY OF YARNS AT LOW (○), MEDIUM (◒), AND HIGH (●) HUMIDITIES; ⊕ REPRESENTS INITIAL FLUIDITY (WIEGERINK[22]).

tively high temperatures, drastic destruction of the material occurs. Destructive distillation in vacuum yields β-glucosan, carbon dioxide, carbon monoxide, water, and small amounts of the gaseous hydrocarbons such as methane and ethylene.

The term "pyrocellulose" has been used to designate the alkali-soluble portion of a cellulose that has been degraded by heat.[23] The reactions of pyrocellulose are similar to oxycellulose in that the former reduces Fehling's solution and shows an enhanced affinity for methylene blue.

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[23] N. Kozhin, *Baumwoll-Ind.*, **6**, No. 3, 29 (1936); *Chem. Zentr.*, **1938, I**, 2096.

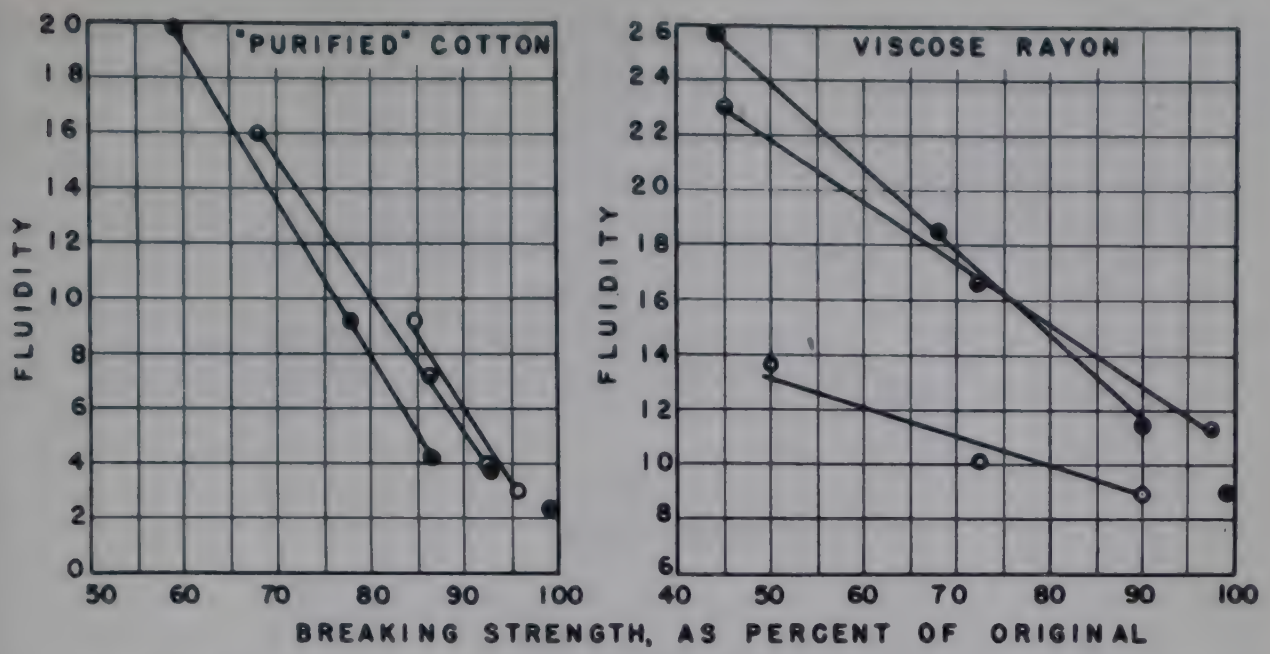


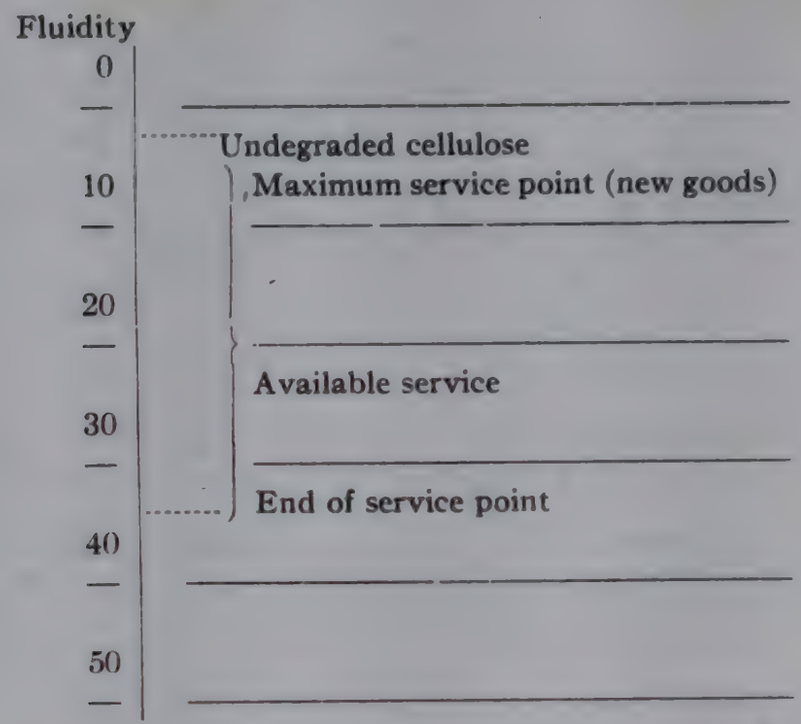
FIG. 29.—RELATIONSHIP BETWEEN FLUIDITY AND BREAKING STRENGTH OF YARNS WHICH HAVE BEEN DRIED AT LOW (○), MEDIUM (◒), AND HIGH (●) HUMIDITIES; ⊕ REPRESENTS INITIAL RELATIONSHIP (WIEGERINK[22]).

(*c*) *Effect of Laundering*

In the laundering of cotton goods, two general types of deteriorations of the material may occur; namely, that produced by abrasion, and that resulting from chemical reactions.[24, 25] The former type can be controlled and minimized by careful handling and is of little importance in so far as any major degradation of the material is concerned. On the other hand, chemical degradation produced by the action of alkalies or bleaching agents such as hypochlorites and hydrogen peroxide may be considerable. Since this type of degradation is principally oxidative in nature, the damage is not always evident and cannot be determined by simple means such as tensile strength measurements (see Section I, 3 of this chapter). A summary of the methods of detecting laundry damage in cotton goods[26] has shown that chemical methods such as solubility in alkali and copper number are also unsuitable, but that the fluidity[24, 26, 27] of the material in cuprammonium solution offers a valuable tool for detecting either hydrolytic or oxidative degradation. Application of this tool to a series of laundering tests indicated that in order to obtain the maximum service, the increase

[24] E. Walter, *Kunstseide u. Zellwolle*, **21**, 402 (1939).
[25] K. Schönleber, *Melliand Textilber.*, **21**, 228 (1940).
[26] *Cowles Technical Tips*, **3**, Nos. 6 and 7 (1935).
[27] R. B. Smith, *Starchroom Laundry J.*, **45**, No. 9, 38, 42 (1938).

in fluidity should not exceed 3.5 rhes for twenty washes. The relation of fluidity to usefulness of cotton materials is shown in the following chart:



A study of the effect of various methods of cleaning on rayons[28] has shown that carbon tetrachloride, naphtha, and water, all containing soap, produce a significant weakening of the materials. The carbon tetrachloride and soap mixture was found to have the least degrading action and naphtha and soap the most degrading action. It may be of interest to note that the acetyl content of acetate rayon was not measurably changed during the cycle of mild alkaline treatments.

In general it can be said that the increase of fluidity of cotton materials due to the action of laundering agents is dependent to a large extent upon the previous treatment of the fabric; for example, fabrics such as curtains which are exposed to light and heat during use have probably been degraded by oxidative processes. The deterioration of this material in a laundering cycle would obviously be much greater than that of the same cotton goods which had not been exposed to light and heat. For such reasons, it has been suggested that the method for cleaning or laundering a particular cotton fabric should be selected according to the type of use to which the material will be put.[29]

It appears that the resistance of rayons to laundering and bleaching processes may depend to some extent on the degree of orientation of the

[28] F. Barr, A. J. Marshall, and R. Edgar, *Am. Dyestuff Reptr.*, **29**, 599 (1940).
[29] T. C. Petrie, *J. Textile Inst.*, **30**, P66 (1939).

material.[30] Repeated swelling during successive launderings may impair the micelle orientation and consequently the laundering of material such as viscose rayon should be carried out at the *p*H of minimum swelling. When a bleaching process is necessary for the adequate cleaning of a rayon, oxygen bleaches rather than chlorine bleaches have been recommended.[31]

[30] E. Elöd, *Melliand Textilber.*, **20**, 57 (1939).

[31] L. Kollmann, *Monatsh. Seide Kunstseide*, **44**, 142, 148 (1939).

Chapter III

STRUCTURE AND PROPERTIES OF CELLULOSE FIBERS

A. X-RAY EXAMINATION

WAYNE A. SISSON

X-ray diffraction analysis, as a research tool for structure determinations, has two closely related fields of application. The first is concerned with the form, properties, and three-dimensional arrangement of atoms and molecules within a single crystal; the second is concerned with the form, arrangement, relative amount, and properties of crystalline aggregates in a polycrystalline material.

Since the x-ray diffraction diagram of most native cellulose fibers consists principally of definite diffraction rings, one is forced to conclude that the major portion of the fiber consists of crystalline celluloses. The first field of x-ray analysis, therefore, as applied to cellulosic materials, is the interpretation of the stereochemistry of the cellulose molecule within the crystal lattice, and in the present section this structure will be referred to as "crystalline structure."

From the fact that cellulose fibers give continuous diffraction rings (*i. e.*, Debye-Scherrer diagrams), a second important deduction may be made: namely, that the crystallinity of the fiber is discontinuous. In other words, a cellulose fiber is not a single crystal; it is a crystalline aggregate. This is definitely proved by the fact that even a single fiber, when photographed by a micro method,[1, 2] gives smooth rings instead of Laue spots. These small crystals of cellulose which build up the cell wall of a fiber will be referred to as "cellulose crystallites," and the material between these crystalline areas as "intercrystalline material." The second field of x-ray analysis, therefore, as applied to cellulosic materials, is the interpretation of the form, arrangement, relative amount, and properties of the cellulose crystallites and their relation to the intercrystalline material. This dual structure built up of crystalline and intercrystalline material will be referred to as "fiber structure."

The crystalline structure of a cellulose fiber, excepting derivatives, may be classified as either (a) native or (b) hydrate. As the name implies, the

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[1] K. Eckling and O. Kratky, *Z. physik. Chem.*, **B10**, 368 (1930).

[2] W. A. Sisson, *Textile Research*, **4**, 286 (1934).

native crystalline structure is found in native fibers; the hydrate structure in mercerized fibers, in regenerated fibers, and in cellulose resulting from the hydrolysis of derivatives.

Likewise the fiber structure may be either of the native or regenerated type. Native fiber structures are closely associated with a biological cell-wall structure which is characteristic for each type of fiber. Since native fibers can be mercerized without disrupting the original cell-wall structure, it is possible to have a fiber, such as cotton, with either a hydrate or a native

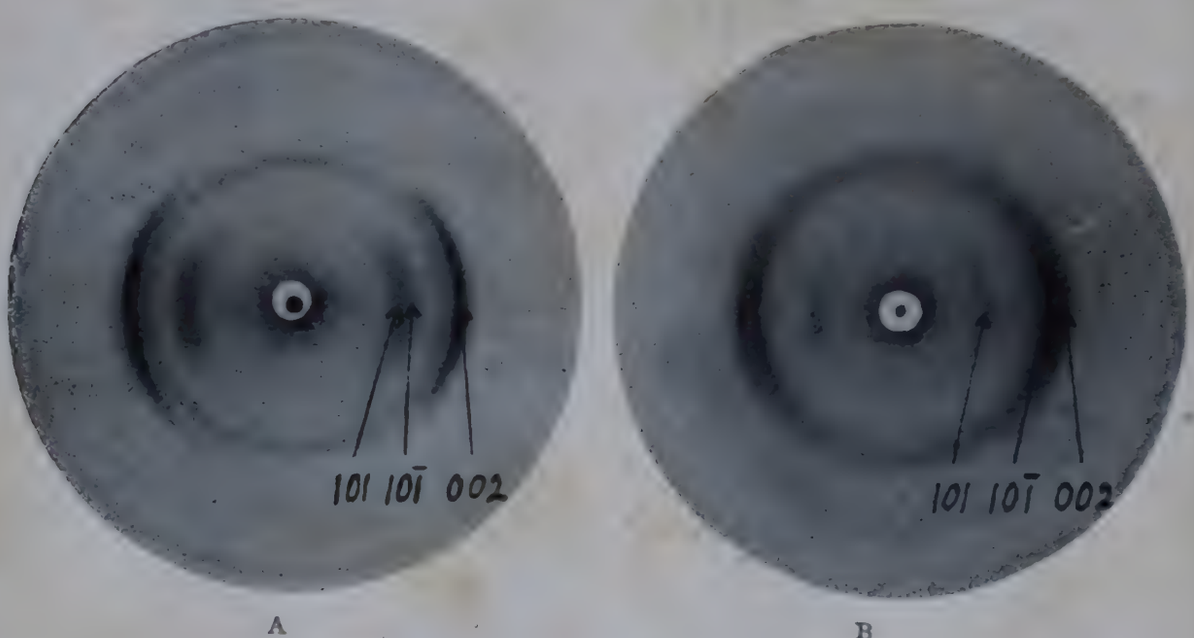

FIG. 1.—X-RAY DIAGRAMS OF COTTON (A) BEFORE MERCERIZATION (NATIVE CELLULOSE), AND (B) AFTER MERCERIZATION (HYDRATED CELLULOSE), SHOWING LOCATION OF THE 101, 10$\bar{1}$, AND 002 DIFFRACTION RINGS.

crystalline structure. Regenerated fibers, on the other hand, always have a hydrate crystalline structure and the fiber structure is a function of the past history of the fiber.

In addition to crystalline and fiber structure information, x-ray diffraction analysis also gives valuable information regarding the mechanism of certain complex chemical reactions, such as derivative formation, swelling, mercerization, crystalline addition compound formation, and hydration These chemical reactions may affect either the crystalline structure or the fiber structure, or both. In studying the reaction behavior of cellulose fibers, therefore, one must take into consideration both the crystalline structure and the fiber structure of the original starting material.

The x-ray diffraction patterns typical of a native cellulose fiber (cotton) and a mercerized fiber (cotton) are shown in Figure 1. These pat-

erns may be described and differentiated one from the other in terms of the following characteristics:

A. Number of diffraction rings.
B. Diameter of each ring.
C. Relative intensity of each ring.
D. Concentration of rings into two or more arcs; orientation.
E. Width or diffuseness of each ring.
F. General scattering or background; amorphous pattern.

The number, diameter, and relative intensity of the diffraction rings are associated with the crystalline structure, while the orientation and width of each diffraction ring and the general scattering are more closely associated with the fiber or membrane structure. It is from these six characteristics that the x-ray information regarding the structure and behavior of cellulose fibers must be obtained.

In general, it is desirable to divide the information obtained into two types, depending on whether or not the fiber has been treated with any of a number of chemical agents. The x-ray data will therefore be presented under two headings: "Cellulose Fiber Structure," which describes the characteristics of the untreated fibers, and "Cellulose Fiber Reactions," which describes those of the treated ones.

1. Cellulose Fiber Structure

The discussion of fiber structure will be divided into four sections (a) crystalline structure, which is described in terms of the unit cell arrangement, (b) micellar structure, which is concerned with the size, shape, and nature of the crystalline areas, (c) amorphous and crystalline areas and their relationship to each other, and (d) orientation or arrangement of the crystalline areas with reference to the fiber axis.

(*a*) *Crystalline Structure*

Our present knowledge regarding the crystalline structure of cellulose has been contributed by a large number of workers over a period of many years. As a background for understanding our present theories, these earlier investigations will be summarized briefly. A detailed survey of the earlier work has been published elsewhere.[3]

It had been known for some time that cellulose fibers were anisotropic,

[3] W. A. Sisson, *Textile Research*, **3**, 242, 295 (1933): **4**, 429 (1934).

but no definite theory regarding the structure had been proposed until 1858 when Nägeli[4, 5] advanced his micelle theory. He postulated that all cellulose fibers were built up of submicroscopic, anisotropic crystalline particles which he called micelles. With the use of polarized light, Gilson,[6] in 1893, first experimentally demonstrated that cellulose was crystalline.

Early X-ray Work. The crystallinity of cellulose was first confirmed by means of the x-ray in 1913 by Nishikawa and Ono.[7] Nishikawa[8] interpreted this pioneer work correctly when he reasoned that any substance which gave a fiber pattern should consist of a number of elementary crystals of a definite structure arranged parallel to the fiber axis.

After Debye and Scherrer had developed the powder method of x-ray analysis, Ambronn[9] in 1916 predicted that if cellulose was a crystalline material it should give a characteristic x-ray diagram. Scherrer,[10] acting upon this suggestion, investigated cellulose with x-rays, but reported that it gave an amorphous pattern. He later repeated this work[11] and obtained a definite crystalline pattern for ramie. In the meantime Hull[12] had independently obtained x-ray diagrams of cellulose fibers.

In order to check the correctness of Scherrer's preliminary report[10] that cellulose was amorphous, Herzog and Jancke in 1920 began an important x-ray investigation of cellulose fibers. They showed that cellulose had a definite crystalline structure which was the same regardless of its source; cellulose from cotton, ramie, wood, jute, flax, and linen all gave identical powder patterns,[13] which supported earlier work regarding the chemical identity of cellulose. If a parallel bundle of ramie fibers was used instead of a powder, a fiber pattern was obtained. They showed that lignified wood gave a cellulose pattern which indicated that lignin was adsorbed on the surface of the cellulose crystallite and not chemically bound.[14] Herzog[15] suggested a rhombic structure and reasoned that, if this symmetry was cor-

[4] C. Nägeli, *Die Stärkekörner*. F. Schulthub, Zürich, 1858.

[5] C. Nägeli and S. Schwendener, *Das Mikroskop*. 2. Aufl., W. Englemann, Leipzig, 1877.

[6] E. Gilson, *La Cellule*, **9**, 337 (1893).

[7] S. Nishikawa and S. Ono, *Proc. Math.-Phys. Soc. Tokyo*, **7**, 131 (1913).

[8] S. Nishikawa, *Proc. Math.-Phys. Soc. Tokyo*, **7**, 296 (1914).

[9] H. Ambronn, *Kolloid-Z.*, **18**, 273 (1916).

[10] P. Scherrer, *Nachr. Ges. Wiss. Göttingen*, **1918**, 98.

[11] R. Zsigmondy, *Lehrbuch der Kolloidchemie*. 3. Aufl., O. Spamer, Leipzig, 1920, p. 408.

[12] A. W. Hull, *Phys. Rev.*, **10**, 661 (1917).

[13] R. O. Herzog and W. Jancke, *Z. Physik*, **3**, 196 (1920).

[14] R. O. Herzog and W. Jancke, *Ber.*, **53B**, 2162 (1920).

[15] R. O. Herzog, *Cellulosechem.*, **2**, 101 (1921).

rect, then the $C_6H_{10}O_5$ units must be linked in pairs by oxygen bonds and that these groups must be repeated regularly.

The first unit cell dimensions to be accepted by later investigators were calculated by Polanyi[16] as 7.9 × 8.45 × 10.2 Å. The 10.2 Å. dimension corresponds to the vertical dimension along the fiber axis, while the 7.9 and 8.45 Å. are horizontal dimensions which form an angle with each other. From the volume of the unit cell, the mass of the glucose unit, and the density of cellulose, Polanyi calculated that a unit cell of these dimensions could accommodate four glucose residues.

By 1923 x-ray workers began to realize the importance of x-rays in studying the physical and chemical behavior of cellulose fibers. For example, Herzog[17] stated that the strength and degree of swelling of cellulose fibers are dependent upon the crystal arrangement, and pointed out that the crystallites of the rayons made at that time lie in all possible directions (random orientation). Hess and coworkers[18] showed that the alkali-soluble portion of hydrocellulose gave the same x-ray pattern as the insoluble fraction. Herzog and Gonell[19] compared the x-ray patterns of plant and animal (tunicin) cellulose and found them to be the same, which confirmed the results of chemists who for a long time had known that the two celluloses gave the same chemical reactions. Herzog and Gonell[20] recognized the fact that rayon fibers gave a crystalline pattern which differed from that of native fibers and that the pattern was of the same type as mercerized fibers. Since mercerization increased the x-ray spacings but not the density of the cellulose, Herzog[21] reasoned there must be a rearrangement of the molecule in the crystal lattice without a change in molecular size. As a result of his x-ray studies of fiber swelling, Katz[22] predicted a future advancement in the knowledge of cellulose structure when he suggested that the cellulose molecule may be larger than the distances indicated by the x-ray spacings.

Unit Cell Structure. Up to this time (1926) most cellulose workers considered the cellulose molecule to be the $C_6H_{10}O_5$ unit,[23] and, although much x-ray information had been obtained, this concept left investigators

[16] M. Polanyi, *Naturwissenschaften*, **9**, 288 (1921).
[17] R. O. Herzog, *Papier-Fabr.*, **21**, Tech.-wiss Tl., 388 (1923).
[18] K. Hess, W. Weltzien, and E. Messmer, *Ann.*, **435**, 1 (1923).
[19] R. O. Herzog and H. W. Gonell, *Z. physiol. Chem.*, **141**, 63 (1924).
[20] R. O. Herzog and H. W. Gonell, *Kolloid-Z.*, **35**, 201 (1924).
[21] R. O. Herzog, *Naturwissenschaften*, **12**, 955 (1924).
[22] J. R. Katz, *Cellulosechem.*, **6**, 37 (1925).
[23] In Polanyi's original paper,[16] however, it was pointed out that the x-ray data were consistent with the viewpoint of long chains common to many unit cells.

at a loss regarding x-ray interpretations. For example, Herzog[24] believed that the cellulose unit cell contained four $C_6H_{10}O_5$ groups which were linked together according to Werner's theory of secondary valence. In 1926, however, new ideas were conceived which acted as a stimulus to the original workers and attracted many new ones into the field. Two outside factors were largely responsible for this renaissance. The first was the progress in the field of sugar chemistry by Haworth, Irvine, Hirst, and others, who succeeded in making clear the configuration of the glucose unit. The other factor was the increase in knowledge regarding the size and shape of atoms and molecules, contributed by the Braggs. This fundamental knowledge, combined with the increased experience in x-ray technique, made possible a more correct interpretation of x-ray patterns which could be checked by the construction of molecular models to demonstrate a three-dimensional picture of the x-ray interpretation. Sponsler and Dore first constructed such a model, and later a more complete model which has remained essentially unchanged up to the present day was developed by Meyer and Mark.

Sponsler and Dore. In 1926 Sponsler[25] put forward the new concept that the cellulose building unit consisted not of independent glucose units but of glucose units connected to form chains which were arranged parallel to the fiber axis. This paper was of importance because it first pointed out that the unit cell, deduced from x-ray data, was only a part of the cellulose molecule. The unit cell dimensions were assumed to be $6.10 \times 5.40 \times 10.25$ Å., with the cellulose chains 6.10×5.40 Å. apart. This gives two $C_6H_{10}O_5$ units within the 10.25 Å. dimension (fiber direction) and four $C_6H_{10}O_5$ units within the unit cell.

Sponsler and Dore[26] later attempted to correlate this model with the chemical and physical properties of cellulose fibers. Three-dimensional molecular models were carefully constructed, based upon the newly published data on atomic radii and interatomic distances and the chemical constitution of sugars, and these models compared with the x-ray data for ramie fibers. They concluded that the ring structure for glucose as advanced by Haworth[27] was in closest agreement with the x-ray data, and that the glucose units were united in chains of indefinite length. Instead of the 1 : 4 linkage favored by Haworth for cellobiose they adopted the system of alternating 1 : 1; 4 : 4 linkages, and, for reasons of symmetry, the beta

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[24] R. O. Herzog, *J. Phys. Chem.*, **30**, 457 (1926).

[25] O. L. Sponsler, *J. Gen. Physiol.*, **9**, 677 (1926).

[26] O. L. Sponsler and W. H. Dore, in *Colloid Symposium Monograph*. Vol. IV, Chemical Catalog, New York, 1926, p. 174.

[27] W. N. Haworth, *Nature*, **116**, 430 (1925).

tructure was given preference to the alpha structure. The axes of the nit cell finally adopted by Sponsler and Dore were $a = 10.8$, $b = 12.2$, nd $c = 10.25$ Å. The recurrency period along the fiber axis ($c = 10.25$ Å.) epends upon the chemical structure of the cellulose molecule and repre- ents the length of two glucose units in the chain, as shown in Figure 2. *Meyer and Mark.* The structure of cellulose as proposed by Sponsler and Dore, however, was not in agreement with the chemical evidence of Ha- vorth[29] who suggested to Meyer that the 1 : 1, 4 : 4 linkage must be re- placed by a 1 : 4, 1 : 4 linkage in the construction of three-dimensional

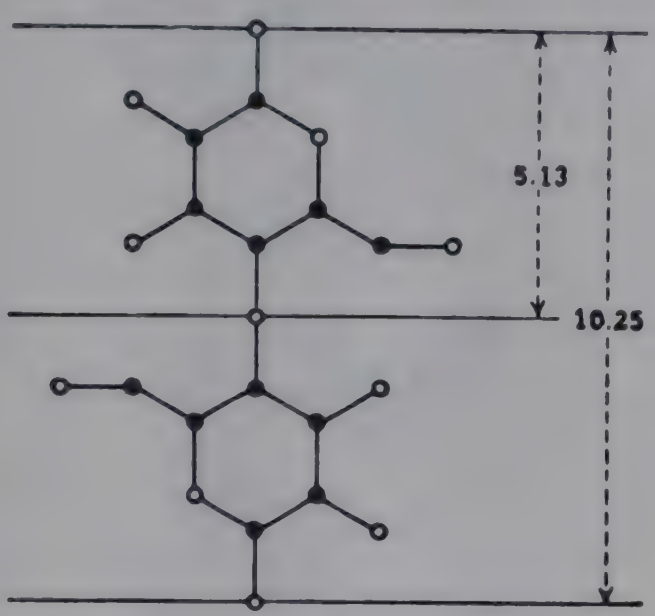

FIG. 2.—TWO GLUCOSE UNITS (SPONSLER AND DORE[28]).

nodels of cellulose. In an attempt to reconcile the x-ray and chemical lata, work was taken up by Meyer in conjunction with Mark, and in 1928 Meyer and Mark[30, 31] showed that a model could be constructed which vas in agreement with both the chemical and with the x-ray data.

The unit cell dimensions previously given by Polanyi in 1921[16] and the eta form of Haworth's cellobiose formula were used by Meyer and Mark n their efforts to fit the glucose units into a basic unit cell. The cellobiose ormula proposed by Haworth[29] is shown in Figure 3. In this model the listance between carbon atoms is 1.54 Å., and the distance between carbon

[28] O. L. Sponsler and W. H. Dore, in *Colloid Symposium Monograph*, p. 192; see ref. 6, p. 208.

[29] W. N. Haworth, *Helv. Chim. Acta*, **11**, 547 (1928).

[30] K. H. Meyer and H. Mark, *Ber.*, **61B**, 593 (1928).

[31] K. H. Meyer, *Z. angew. Chem.*, **41**, 935 (1928).

and oxygen atoms is 1.35 Å. The length of the cellobiose unit is thus 10.3 Å. The x-ray cellulose fiber diagram calls for a diagonal screw axis with repeat patterns every 10.3 Å. Since the lower half of the cellobiose unit is turned through 180° this cellobiose unit thus fulfills the requirement for a diagonal screw arrangement, and allows for the 1 : 4 linkage in agreement

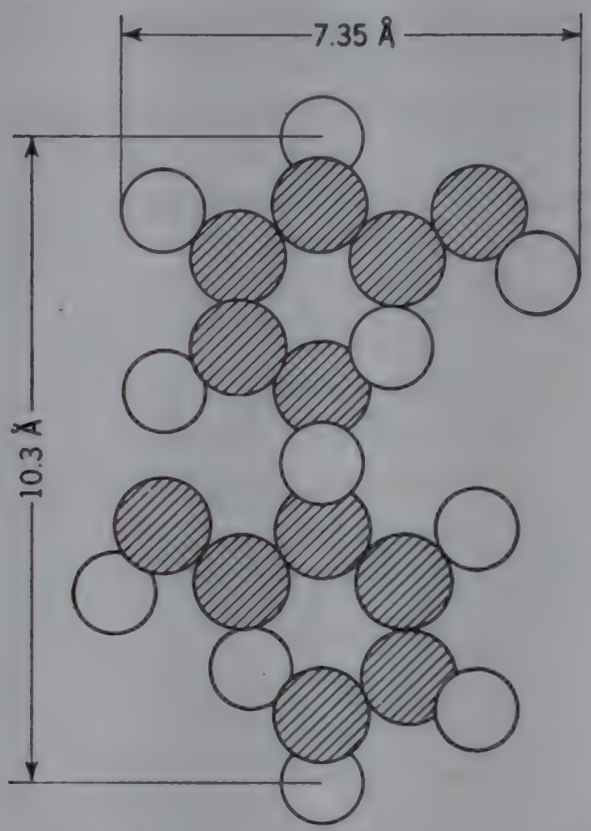

FIG. 3.—CELLOBIOSE UNIT ACCORDING TO HAWORTH (MEYER AND MARK[32]).

The shaded circles indicate the carbon atoms; oxygen atoms are represented by open circles, while hydrogen atoms are omitted.

with chemical evidence. A diagram of the unit cell was put forward by Meyer and coworkers[33, 41, 42] (Fig. 4). The dimensions are $a = 8.35$, $b = 10.3$, and $c = 7.9$ Å. The planes of the glucose units lie in the ab plane of the unit cell which gives the strongest diffraction lines, and the axes of cellobiose units run parallel to the b axis of the unit cell. Each corner and the center of the unit cell is occupied by a cellulose chain. Since the two glucose units at each corner are shared by the four neighboring unit cells, this leaves two glucose units per unit cell for the eight corners, which together with the two in the center gives a total of four glucose units per unit cell. The unit

[32] K. H. Meyer and H. Mark, *Aufbau der hochpolymeren organischen Naturstoffe*. Akademische Verlagsgesellschaft m.b.H., Leipzig, 1930, p. 110.

[33] K. H. Meyer and H. Mark, *Z. physik. Chem.*, **B2,** 115 (1929).

cell is merely the geometrical pattern or arrangement of the glucose units which repeats itself in all directions and is not to be confused with the cellulose molecule or micelle.

With the exception of dimensions and the 1 : 4 linkage, the model of Meyer and Mark is essentially the same as that of Sponsler and Dore. Both agree on the important concept of long cellulose chains, composed of

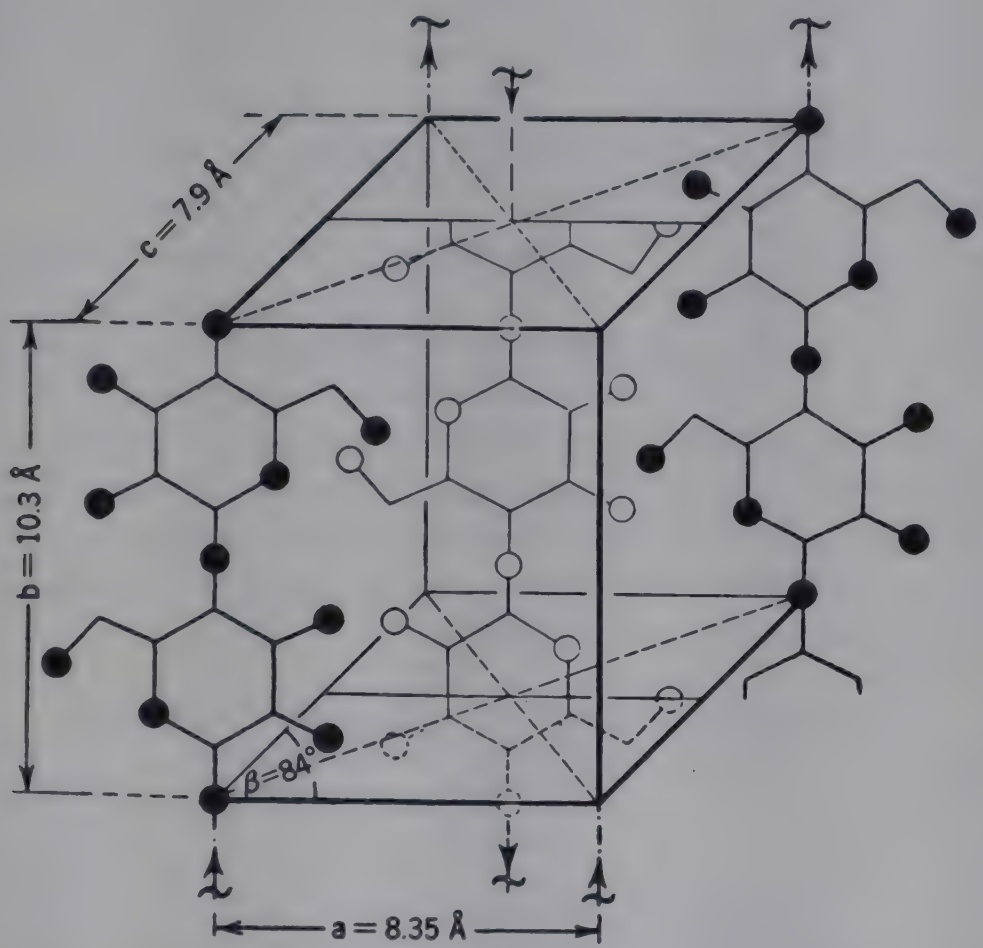

FIG. 4.—UNIT CELL OF NATIVE CELLULOSE (MEYER AND COWORKERS[33, 41, 42]).

glucose units bound by primary valence bonds, which run parallel to the *b* axis of the unit cell and which are stabilized laterally with reference to each other by secondary valences. Bragg[34, 35] pointed out that the unit cell of Meyer and Mark and of Sponsler and Dore are mathematically the same, the diagonal of the former being the same as the side of the latter. In comparing the two unit cells, however, it must be remembered that Sponsler and Dore used *c* and Mark and Meyer *b* to designate the axis parallel to the

[34] W. H. Bragg, *Nature*, **125**, 634 (1930).
[35] O. L. Sponsler, *Nature*, **125**, 633 (1930).

cellulose chains. The physical and chemical properties of cellulose which depend upon crystal structure are thus the same for either model.

Mercerized Cellulose. As previously pointed out, Herzog and Gonell[20] early recognized the fact that rayon and mercerized fibers gave a crystalline pattern which differed from that of native fibers. Since the x-ray spacings were increased but not the density of the cellulose, Herzog[21] reasoned that there must be a rearrangement of the molecule within the crystal lattice. Subsequent work by Herzog and by Katz, Vieweg, and Mark gave much information regarding the conditions under which this mercerized or hydrate crystalline form of cellulose is produced, but no real progress regarding its crystal structure was made until the native structure had been worked out by Sponsler and Dore and by Meyer and Mark.

Sponsler and Dore[36] found that upon mercerizing ramie fibers (treatment with sodium hydroxide followed by washing), the dimension of the unit cell parallel to the cellulose chains remained unchanged while the lateral axes were enlarged. They interpreted this to mean that the chains of glucose units have been shifted laterally but have remained unbroken.

The unit cell structure of mercerized cellulose was first worked out in detail by Andress[37] and found to belong to the same crystal system (monoclinic) as native cellulose. The differences in unit cell dimensions of native and mercerized cellulose are listed below.

COMPARISON OF NATIVE AND MERCERIZED CELLULOSES

Axis	Native	Mercerized
a	8.35 Å.	8.1 Å.
b	10.30 Å.	10.3 Å.
c	7.90 Å.	9.1 Å.
β	84°	62°

A view of the two unit cell arrangements is shown in Figure 5. It will be noticed that the planes of the molecular chains have shifted as a result of the glucose units rotating about 30° around their chain axis. The shift makes the hydroxyl groups more accessible, which is in agreement with the observed increased chemical reactivity of mercerized cellulose. Herzog and Jancke[38] have suggested that the mercerized form is the more stable since it is the form assumed by cellulose at normal temperatures after swelling or after regeneration from solution or from a derivative.

[36] O. L. Sponsler and W. H. Dore, *J. Am. Chem. Soc.*, **50**, 1940 (1928).
[37] K. R. Andress, *Z. physik. Chem.*, **B4**, 190 (1929).
[38] R. O. Herzog and W. Jancke, *Z. physik. Chem.*, **A139**, 235 (1928).

Later Developments. The first unit cell structures proposed by Polanyi[16] and later by Sponsler and Dore[26] for native cellulose were rhombic. The cell worked out by Meyer and Mark[33] was monoclinic. More recently (1937) a new type of monoclinic cell has been suggested by Sauter.[39] From a study of highly oriented samples of native cellulose, Gross and Clark[40] conclude that a monoclinic cell with the dimensions $a = 8.35$ Å., $b = 10.3$ Å., $c = 7.95$ Å. and the angle between a and c, $\beta = 84°$, is in best agreement

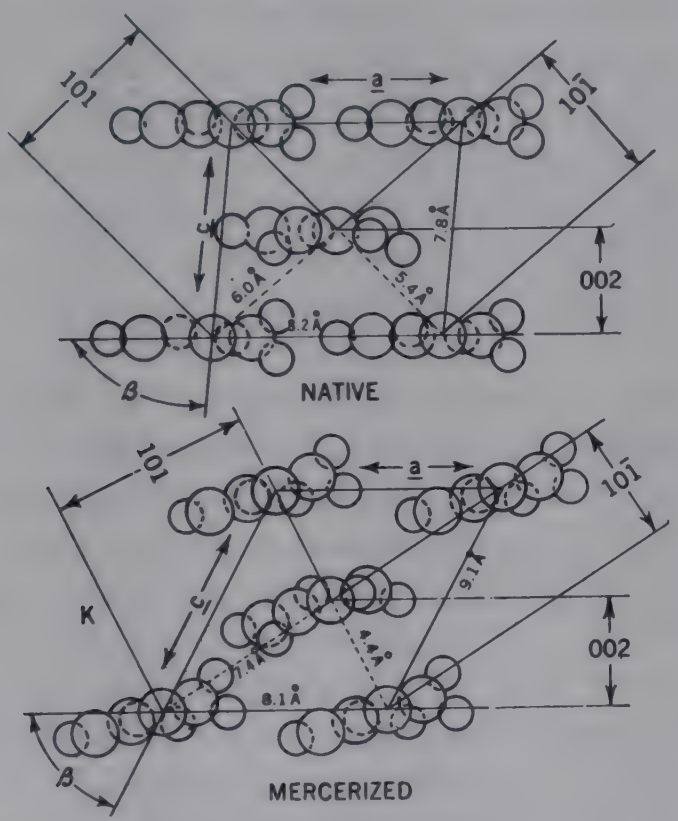

FIG. 5.—VIEW DOWN *b* AXIS OF UNIT CELL OF NATIVE AND MERCERIZED CELLULOSE SHOWING THE LOCATION OF *a* AND *c* AXES, ANGLE β, AND THE 101, 10$\bar{1}$, and 002 PLANES (ANDRESS[37]).

with the experimental evidence. In considering the crystalline structure of cellulose, however, it must be remembered that owing to the absence of single crystals the unit cell structure cannot be conclusively defined. A model, such as shown in Figure 4, represents the most logical structure on the basis of the existing data.

By referring to Figure 4, it can be seen that the unit cell is composed of two sets of chains each having a twofold screw axis parallel to the *b* axis of

[39] E. Sauter, *Z. physik. Chem.*, **B35**, 83 (1937).
[40] S. T. Gross and G. L. Clark, *Z. Krist.*, **A99**, 357 (1938).

the unit cell. Meyer and Mark in their original work assumed these two sets of chains, which are independent of each other, to run in the same direction. Meyer and Misch[41, 42] later reasoned that the cellulose chains in a newly coagulated viscose solution should lie in both directions. Since regenerated and mercerized celluloses have the same structure and since it is not likely that the mercerizing process would cause the reversion of cellulose chains, it would seem logical to assume alternating orientation of chains in native cellulose. They investigated the x-ray diagram intensity of both fibrous and powdered cellulose and found that the calculated intensities required by the new model were in good agreement with the experimental observations. Using the unit cell dimensions of Meyer and Misch, Lyons[43] has calculated that the density of crystalline cellulose should be 1.582 g./cc. This is higher than the 1.5 g./cc. usually accepted for cellulose, but agrees with the value obtained when the void spaces are filled with helium so as to correct for the intercrystalline and void spaces in cellulose fibers.

Further information regarding the nature of the forces which hold the lattice structure together has been reviewed by Mark.[44] By referring to Figure 4, it is obvious that in the direction of the *b* axis the glucose units are held together by 1 : 4 glucosidic bonds. Along the *a* axis the glucose rings are only separated by a distance of 2.5 Å. In most other organic crystals two oxygen atoms belonging to different molecules do not approach each other closer than about 3.0 Å. if only van der Waals' forces are acting between them. This suggests that stronger forces are acting, and it is reasonable to assume that a hydrogen bond is established between the two oxygen atoms. This would explain the comparatively tight packing in the *ab* plane in the direction of the *a* axis, and at the same time offer an explanation for the fact that swelling agents disrupt this bond to form swelling compounds. Along the *c* axis the nearest distance of atomic centers is about 3.1 Å. This corresponds closely to the distance to be expected if van der Waals' forces hold the lattice together in this direction. As pointed out by Mark,[44] cellulose may be regarded as a combination of a chain lattice and a layer lattice. The strongest forces are the main valence chains along the *b* axis, but the hydrogen bond nets along the *a* axis (*ab* plane) are also comparatively large. Perpendicular to the *ab* plane, however, weaker van der Waals' forces are acting, and the spacings between the atoms in this

[41] K. H. Meyer and L. Misch, *Ber.*, **70B**, 266 (1937).
[42] K. H. Meyer and L. Misch, *Helv. Chim. Acta*, **20**, 232 (1937).
[43] W. J. Lyons, *J. Chem. Phys.*, **9**, 377 (1941).
[44] H. Mark, *Chem. Revs.*, **26**, 169 (1940).

irection are large. By referring to Figure 5, it is obvious that the spacings nd force relationships of the chains in native and mercerized cellulose are ifferent. Thus it might not be too far-reaching to say that the fact that ellulose chains at different distances apart are held together by three differnt kinds of forces in three different directions in space may be responsible in art for the interesting and important properties which cellulose exhibits uring its reactions in the solid state.

(*b*) *Micellar Structure*

In a cellulose fiber the three-dimensional or unit cell arrangement of the glucose units, discussed in the previous section, is repeated in all directions o build up a crystalline area. As previously pointed out, a cellulose fiber is ot a single crystal; it is a crystalline aggregate consisting of small crystal areas (crystallites) separated by amorphous or intercrystalline areas. The erm crystallite is used without connoting any particular size, shape, or nature of the boundaries between the crystalline areas, while the term micelle is used to designate a definite concept of the crystallite.

By most workers, the dimensions of the crystallite have been assumed to be larger than the distances directly measured by x-rays and smaller than those visible in the microscope. Likewise, all of the chemical data which measure the average size of the micelle or macromolecule as it exists in solution rest upon acts of disruption of the original fiber, and, since it is not definitely known what happens during the solution process, it is difficult to extrapolate the results back to the untreated fibers. As a result there has been much discussion, and many ideas have been advanced, regarding the nature of the crystallite. It is of interest to review the development of the more interesting ideas in this connection and to outline briefly five of the theories which have been advanced. These theories will be referred to as (1) the micellar theory, (2) the continuous structure theory, (3) the secondary structure theory, (4) network or fringe micellar theory, and (5) the cellulose particle theory.

Micellar Theory. The micellar theory was first advanced by Nägeli[4, 5] in 1858. He postulated that all cellulose fibers were built up of submicroscopic, anisotropic crystalline particles which he called micelles. His concept of a micellar structure was based upon polarized light and upon swelling studies. He considered micelles to be discrete particles, between which water entered to produce swelling. Nägeli was able to explain many properties of cellulose which could not then be explained by any other theory, but his theory was not generally accepted at that time. Later,

when x-ray workers found cellulose to be definitely crystalline, the micellar theory was again revived, and Scherrer[10] in his early work refers to the micelles being oriented parallel to the fiber axis. Herzog[45] considered the

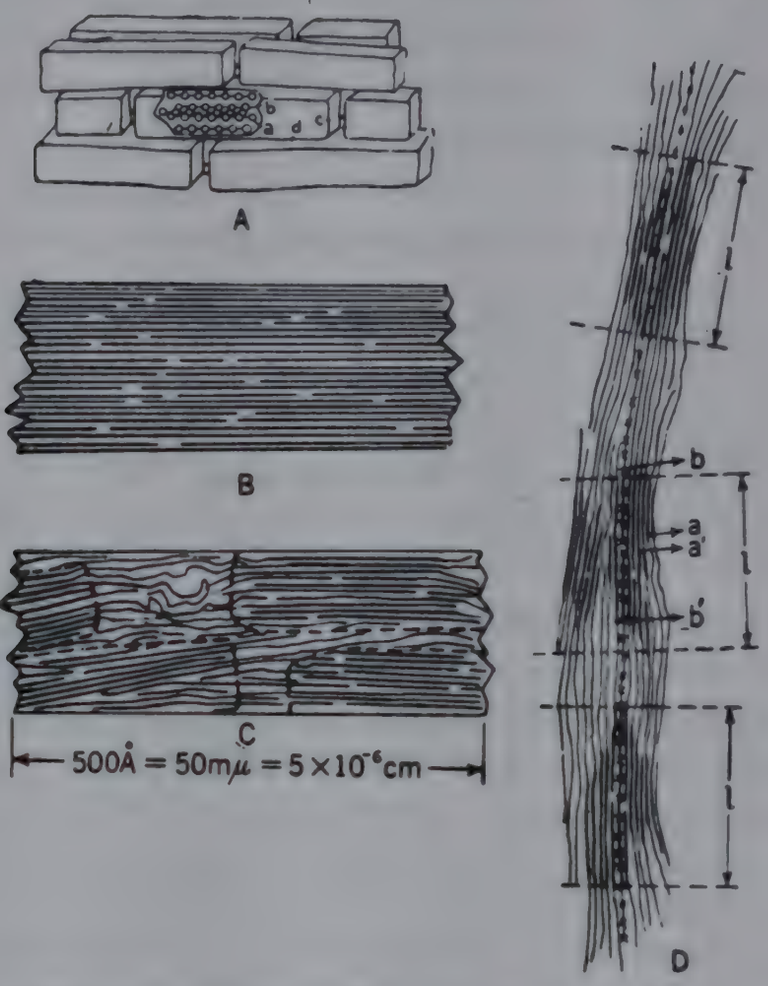

FIG. 6.—SCHEMATIC REPRESENTATION OF SEVERAL POSSIBLE CRYSTALLITE STRUCTURES (MARK[46]).

(A) Micellar theory (Seifriz[47]); (B) continuous structure theory; (C) fringe micellar theory. How main valence chains pass through more than one micelle (fringe micellar theory) is shown in (D).

a, *a'*, *b'*. Molecule ends inside the crystallized region of one micelle.

b. Molecule end outside the crystallized region.

l. Length of crystallized region.

fiber to be a two-phase system, consisting of a crystalline and an intercrystalline material, and Sponsler[48] pointed out that the blurred lines produced from cellulose must be due to the small size of the crystallites.

The first workers to adopt and expand the micellar theory, in an attempt

[45] R. O. Herzog, *Ber.*, **58B**, 1254 (1925).

[46] H. Mark, *J. Phys. Chem.*, **44**, 764 (1940).

[47] W. Seifriz, *Am. Naturalist*, **63**, 423 (1929).

[48] O. L. Sponsler, *Phys. Rev.*, **23**, 662 (1924).

to explain the x-ray as well as other physical and chemical data, were Meyer and Mark.[30, 33] They emphasized the fact that many of the properties of cellulose are due not to cellulose molecules, but to molecular aggregates or micelles made up of parallel cellulose chains. The micelles are submicroscopic in size and are much longer than they are thick. They are arranged with their long axis roughly parallel or spiral with respect to the fiber axis and are held together by intermicellar forces, which are similar in nature to van der Waals' forces. No definite conclusions were reached in the early work regarding the form of the micelle, but later Hengstenberg and Mark[49] estimated the size of the micelle in ramie to be approximately 50 Å. in diameter and over 600 Å. long.

The earlier concepts of micellar structure, such as represented in Figure 6A,[47] imply an arrangement in which the micelles may be compared to the bricks in a wall, each micelle overlapping its neighbor and bound to it by intermicellar forces. Since the x-ray diagram of most cellulose fibers shows the presence of amorphous material, Herzog[50] has suggested that this exists as a cementing material, a *Kittsubstanz* which exists between the micelles. This picture involves a very distinct difference between the space inside the micelle and that outside. Intermicellar and intramicellar spaces are to be clearly distinguished in their behavior toward chemical reagents.

Since 1930 considerable emphasis has been placed on "long-chain" or "macro" molecules. Ultracentrifugal, viscosity, and related physiochemical methods all indicate the molecular cellulose chain to be more than ten times longer than the estimated size of the micelle. As a result there evolved a new concept of the cellulose crystallite which was in direct contrast to the micellar theory. This concept will be referred to as the "continuous structure" theory.

Continuous Structure Theory. Although the x-ray data imply a discontinuous crystalline structure for cellulose, there is, however, no proof that the discontinuity consists of discrete, crystalline particles or micelles as originally postulated by the micellar theory. Peirce,[51] Neale,[52] Sponsler,[53] and Astbury[54] have argued that it is more in conformity with the evidence to suppose that the molecular order only approximates to crystalline perfection, being interspersed with partial local discontinuities. Likewise,

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[49] J. Hengstenberg and H. Mark, *Z. Krist.*, **69**, 271 (1928).
[50] R. O. Herzog, *Kolloid-Z.*, **39**, 98 (1926).
[51] F. T. Peirce, *Trans. Faraday Soc.*, **29**, 50 (1933).
[52] S. M. Neale, *Trans. Faraday Soc.*, **29**, 228 (1933).
[53] O. L. Sponsler, *Quart. Rev. Biol.*, **8**, 1 (1933).
[54] W. T. Astbury, *Trans. Faraday Soc.*, **29**, 193 (1933).

the work of Staudinger[55, 56] naturally implies a fiber molecule much larger than the estimated micellar dimensions, and it is assumed that these macromolecules exist in the original native fiber as part of a continuous structure.

In order to explain the x-ray data, it is not necessary to assume chains broken lengthwise or separated sidewise to form individual crystals. If the crystalline regularity of the cellulose chains were interrupted by regions where the chains are not sufficiently close or regular to form a crystal lattice, then these regions would produce in the x-ray diagram the same effect as though they were amorphous material separating well-defined crystallites. In the cell wall of a fiber those regions which possess a definite crystalline regularity of cellulose chains may be considered as "crystallites"; at other places, where the chains have an irregular arrangement, these areas may be considered as "amorphous" or "intercrystalline" cellulose material.

The physical properties of the native fibers are better explained on the basis of a continuous structure (Fig. 6B) than on a micellar structure. For example, the fact that the tensile strength of cotton is high and increases with increasing moisture is accounted for on the assumption that the molecular chains themselves are broken when a cotton fiber is ruptured. The observations on the dry and wet tensile strengths of rayon, however, are better interpreted by the micellar theory. Furthermore, the micellar theory more readily explains the x-ray data, but it is weak when explanations are required of the difference between the physical and chemical properties of the natural fibers and rayon, and also for certain other properties of the native fibers.

An attempt has been made[57] to compromise between the conception of discrete micelles, on the one hand, and the existence of a continuous structure, on the other. This theory, which is designed primarily to explain the properties of native fibers, will be referred to as the "secondary structure" theory.

Secondary Structure Theory. It is impossible to explain the physical properties of a single crystal on the basis of the unit cell arrangement of ions or molecules and the forces bonding them together. Zwicky,[58, 59]

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[55] H. Staudinger, *Die hochmolekularen organischen Verbindungen*. J. Springer, Berlin, 1932.

[56] H. Staudinger, *Ber.*, **70B**, 2514 (1937).

[57] W. A. Sisson, *Textile Research*, **6**, 143 (1936).

[58] F. Zwicky, *Proc. Natl. Acad. Sci. U. S.*, **15**, 253, 816 (1929).

[59] F. Zwicky, *Phys. Rev.*, **38**, 1772 (1931); **40**, 63 (1932); **43**, 765 (1933).

herefore, has postulated that superimposed upon the unit cell lattice there s another lattice on a much larger scale, consisting of crevices or cracks vhich give the crystal a secondary structure. A single crystal consists of a atticework of ions or molecules upon which is superimposed a coarser tructure consisting of crevices. This view has been shown to be consistent vith the low tensile strength and the diffusion through single crystals, etc.

Likewise, most of the important physical properties of cellulose fibers, such as tensile strength, elasticity, swelling, and shrinkage, are not dependent upon the unit cell structure and the forces bonding the molecules together into a crystal lattice, but upon a discontinuous crystal structure. It would seem logical, therefore, to assume that the micellar properties of cellulose may be explained on the basis of Zwicky's theories for a single crystal. The secondary structure of crystalline cellulose may be roughly compared with the surface of a dried pond, covered with cracks and crevices, with the exception that the principal crevices run parallel to the cellulose chains and are partly occupied by amorphous materials. This type of structure would thus give many long fibril-like fragments when the fiber is disintegrated. This concept is in agreement with the data on the dispersion and modification of cellulose which are difficult to explain on the basis of a micellar theory, since modification and degradation are known to proceed gradually and not in uniform steps.

Micellar Network or Fringe Micellar Theory. In recent years new experimental evidence, especially in connection with regenerated cellulose and with synthetic high-polymeric substances, has brought about the abandonment of the earlier pictures of micellar structure and the substitution of a new concept, which will be referred to as the "network" or "fringe micellar" theory (Figs. 6C and 6D). This concept may be considered as a compromise between an extreme micellar structure and an extreme chain or continuous structure.[47]

According to this theory the crystalline areas are not clearly separated from each other by a distinct micellar surface, but rather by an area of partially parallel but disorganized chains. Long crystalline particles are postulated whose outer form is irregular, and defined, especially at the ends, by the projecting, irregularly arranged, primary valence chains which may pass through several micelles and thus tie them together. This gives a net-like structure in which chains occur that are partly crystalline and partly amorphous. Furthermore, it has been proposed that the crystallites are formed as a result of the free rotation of glucose units around their oxygen bridges; crystalline areas result when a group of chains coalesce in a three-dimensional arrangement, while amorphous regions are produced when

there is a divergence from the crystalline arrangement. As a consequence cellulose gives a discontinuous crystalline pattern.[60]

This theory accounts for the deformation behavior of regenerated cellulose and the change in mechanical properties which occur during spinning and stretching.[61] Assuming a normal chain-length distribution, it also explains why the average chain length above a certain point no longer has a measurable influence on the tensile strength of rayons, since the chain ends are distributed at random in the crystalline areas and their weakening effect is reduced by the crystallization forces. If the length of the chains, however, approaches that of the micelle, then the ends will more frequently coincide with the amorphous regions with the result that the tensile strength will be more dependent upon secondary valence forces which are especially sensitive to water.

Cellulose Particle Theory. The work of Farr and Eckerson[62] and subsequent work by Farr,[63] showing the formation of cellulose fibers from microscopic particles of uniform size in linear arrangement, led to the suggestion that the cellulose particle might be substituted for the micelle in the current interpretation of x-ray diffraction data on native fibers.[64, 65] These particles, as observed in young cotton fibers with the aid of the microscope, are ellipsoidal in shape (1.1 μ thick and 1.5 μ long), and appear to be covered with a coat of noncrystalline substance. The assumption that they are fundamental building units is based upon the fact that they may be observed in the living cytoplasm of young cotton fibers.[62] During fiber growth, the particles unite end to end to form fibrils, which are deposited in a spiral arrangement to build up the mature cell wall. Many of the x-ray requirements for a cellulose crystallite appear to be fulfilled by the particle. For example, the size of the cellulose particle is within the limit necessary to give the Debye-Scherrer pattern characteristic of cellulose, and, since the cellulose chains are arranged parallel to the long axis of the particle, the concept of particles arranged end to end to build up the fibril would account for the fiber patterns of well-oriented native cellulose fibers, as will be brought out in a later discussion on orientation. The particle theory is useful in explaining the formation of cellulose and the morphological structure of native fibers, but it is not in agreement with many of

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[60] O. Kratky and H. Mark, *Z. physik. Chem.*, **B36**, 129 (1937).
[61] P. H. Hermans, *J. Phys. Chem.*, **45**, 827 (1941).
[62] W. K. Farr and S. H. Eckerson, *Contrib. Boyce Thompson Inst.*, **6**, 189 (1934).
[63] W. K. Farr, *J. Phys. Chem.*, **41**, 987 (1937); **42**, 1113 (1938).
[64] W. A. Sisson, *Textile Research*, **5**, 119 (1935).
[65] W. A. Sisson, *Chem. Revs.*, **26**, 187 (1941).

the chemical properties of cellulose and it appears to be of little value in connection with regenerated fibers.

Comparison of Theories. In attempting to explain the x-ray, physical, and chemical behavior of cellulose, on the basis of a discontinuous crystalline structure, it appears impossible to use the same theory for both native and regenerated fibers. To the cellulose chemist, the morphological structure of native fibers is an unwanted complication in the study of cellulose in terms of molecular units, but nevertheless it is a factor which must be considered in any comparison of native and regenerated fibers. It is apparent that the original morphological structure of the fiber is wholly or partially disrupted by the solution process (*e. g.*, cuprammonium and viscose) and that upon regeneration a recrystallization must take place, resulting in a redistribution of crystalline and intercrystalline areas as well as a different crystalline structure (hydrate). It would appear necessary, therefore, to have at least two theories of crystallite structure: one for native and one for regenerated fibers. Which theory is the more plausible is a matter of personal opinion.

In the light of present information, it is the author's opinion that the fringe micellar theory gives a quite satisfactory explanation of the behavior of regenerated fibers. With respect to native fibers the situation is less satisfactory. Evidence is accumulating that the fibril is the characteristic unit of structure in this case, but the exact nature of the fibril is not known. It is possible that the formation of fibrils from discrete particles during fiber growth will be found to conform with the facts, but it is yet unexplained how the particles become joined with one another to form the fibril. A further complication is the relationship of the relatively large (1.1 μ diameter) fibril formed from the particles to the much smaller fibrils which are shown in the electron microscope. If the particle formation of cellulose is accepted, it appears necessary to assume a highly swollen state for the particle as it exists in the cytoplasm. Since the identity of the particle is lost in that of the fibril during fiber growth, it seems logical to assume that the properties of a mature fiber are more directly related to the fibril structure than to the particles which originally formed the fibril.

From comparative x-ray and microscopic studies on a membrane such as *Valonia* where the fibrils possess a definite biaxial orientation in the cell wall, it is possible to draw certain conclusions regarding the crystalline structure of the fibril.[66] First, the cellulose chains (*b* axis of the unit cell) run parallel to the long axis of the fibril. Whether a single chain runs the

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[66] W. A. Sisson, *Contrib. Boyce Thompson Inst.*, **12**, 171 (1941).

entire length of the fibril or only part of the way, is not known. Second, the various crystallographic planes of the unit cell extend continuously in the same direction throughout the fibril. From the intrinsic nature of the x-ray data it is impossible to say definitely that the fibril does not contain still smaller crystalline areas or fibrils, but, if such is the case, the present data impose the condition that these smaller units (crystallites) have a perfect three-dimensional orientation within the fibril.*

Space does not permit an adequate discussion of the role of the cellulose crystallite in many chemical reactions. It should be emphasized, however, that the term crystallite refers only to the physical structure or arrangement of the long-chain molecules in the solid state resulting from the manner of formation of the cellulose in the plant and in no way conflicts with the concept of cellulose chains existing as individual units in the dissolved state. Crystalline and amorphous cellulose (of equal chain length) cannot be distinguished in the completely dissolved state, but they do differ in their rate and degree of solution. Any dense element of structure in the fiber such as the fibril, being a relatively large, highly crystalline aggregate of cellulose chains, would be naturally more resistant to attack than would be the less organized, intercrystalline areas. The crystalline region can be penetrated by chemical reagents as evidenced by the formation of cellulose derivatives in the solid state. Furthermore, certain swelling agents are able to penetrate the crystalline region to form swelling compounds (see later discussion on swelling) and eventually to produce solvation of the long-chain molecule; the degree depends upon the nature of the swelling agent, the concentration, agitation, etc. There is some evidence for the fibril as a physical unit in highly swollen fibers, or in incompletely dispersed solutions, and it is probable that a large number of crystallite remnants in a highly swollen or gel state pass through concentrated commercial solutions, such as viscose, and serve as crystallization nuclei in the regenerated fiber.

(*c*) *Amorphous and Crystalline Areas*

As previously pointed out, a crystallite may be defined as an area in which a highly geometrical order (unit cell structure) prevails, and the dis-

* Note added to proof, Jan. 25, 1943. Since this manuscript was written in late 1941, electron microscope papers have appeared (*e. g.*, see Barnes and Burton, *Ind. Eng. Chem.*, **35**, 120 (1943)) which indicate that the chief characteristics of many published photomicrographs of cellulose particles and fibrils have been determined by diffraction effects. The electron microscope shows disintegrated cellulose to consist of fibrils which are much smaller than that indicated by the microscope.

tance between side groups of neighboring chains is governed by strict laws. The presence of crystalline cellulose may be identified by the fact that it gives definite x-ray diffraction lines. Amorphous material, on the other hand, may be identified by the fact that it does not give definite diffraction lines, but an amorphous area cannot be defined as a region in which there is complete lack of geometrical order. Owing to the strong crystallization tendency of cellulose, the probability of a completely disorganized state is very small, and most amorphous areas must be considered as regions having an intermediate state of organization.

In considering the fiber structure of cellulose the discussion will be grouped under three headings: (1) native fibers, (2) regenerated fibers, and (3) cellulose derivatives.

Native Fibers. The number, diameter, and relative intensity of the x-ray diffraction rings appear to be constant for all native cellulose fibers. Since these characteristics of the x-ray pattern are associated with the crystalline structure, it may be concluded that the crystalline structure of native cellulose is the same regardless of the fiber in which it originates. The only known exception is the large, single-celled, marine plant, *Halicystis*,[67] which contains cellulose in the hydrate or mercerized form rather than the usual native form.

Crystallinity. The degree of perfection of cellulose crystallinity varies for different fibers, as indicated by the definition or sharpness of the diffraction rings. For a given sample size and slit system the x-ray diffraction lines should have a definite width, but in most cellulose patterns this line breadth is greater than that theoretically expected. In some of the bast or lignified fibers, such as ramie or wood, the lines are very broad; in cotton they have a medium width, while in *Valonia* they are very sharp. Furthermore, in many of the fibers which show orientation, the diffraction lines arising from planes parallel to the *b* axis (equatorial lines) have a greater width than the lines arising from planes perpendicular to the *b* axis (meridian lines).

This abnormal equatorial line breadth of cellulose diffraction patterns may be explained in several ways; it may be due to crystal size, strain, impurities, imperfectly formed crystals, or to a combination of any of these. From calculations based upon a theoretical relationship between crystal size and line breadth, Hengstenberg and Mark[49] have estimated the size of the micelle in ramie to be approximately 50 Å. in diameter and over 500 Å. long. The line breadth method, which has been employed with success in estimating the particle size of many colloidal materials, is only valid provided other

[67] W. A. Sisson, *Science*, **87**, 350 (1938).

factors are absent, and this is a difficult assumption to make in the case of cellulose fibers. For example, it is well known that a condition of strain within a crystal will produce a broadening of the diffraction lines,[68] and the effect of a small amount of foreign atoms included in the crystal lattice in producing a broadening of the lines has been clearly demonstrated in the case of metals.[69] More recently Meyer[70] has estimated 1000 to 1500 Å. as the minimum length of the micelle.

Amorphous Material. In addition to crystalline cellulose there is also present in most fibers a certain amount of amorphous material, as indicated by a general fogging in the x-ray diagram. This fogging, which varies in its nature and amount from fiber to fiber, often approaches a broad amorphous band similar to that of a homogeneous liquid. In other fibers, such as wood, it takes the form of a disk extending to the central beam, which is typical of a heterogeneous amorphous material. In cotton the fogging is very faint, while in some of the woody or lignified tissues it may almost completely mask the crystalline cellulose pattern.

Some of the fogging may be due to amorphous cellulose, but in native fibers most of it comes apparently from the noncellulosic constituents, since the fogging is usually reduced by cellulose purification treatments. There is no reason, however, to believe that the amorphous cellulose and the noncellulosic constituents exist as distinctly separate phases; instead, as will be discussed later, these are indications of a gradual transition from amorphous to crystalline areas with the transition boundaries consisting of a mixture of cellulose and noncellulosic molecules.

Since many noncellulosic materials are so closely associated with cellulose during its formation in the cytoplasm, it is possible that there may be a sort of mixed crystallization of the cellulose with noncellulosic materials at the surface of the crystallite. One would not expect the surface of the crystallite, molecularly speaking, to be as smooth as the surface of crystals which are built up of small molecules held together by secondary valence forces. On the contrary, one would expect the long primary valence cellulose chains to protrude at the surface and especially at the ends of the crystallite to give a fringe structure. This type of structure would allow the polar hydroxyl groups of the protruding chains to become closely associated with other hydrophilic cytoplasmic constituents during cellulose formation in the growing fiber. The structure would thus vary from crystalline cellu-

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[68] C. S. Barrett, *Metals & Alloys*, **5**, 154, 170, 196 (1934).

[69] W. P. Davey, *Crystal Structure and Its Application*. McGraw-Hill, New York, 1934.

[70] K. H. Meyer, *Ber.*, **70B**, 266 (1937).

lose in the interior of the crystallite to an amorphous mixture of cellulose and noncellulosic materials at the outer surface. This outer surface would try to crystallize as well as possible, producing a distortion and lattice strain which would extend throughout the crystallite. For example, it is possible that the close association of lignin and other noncarbohydrates with cellulose may be explained in terms of a mixed crystallization at the surface of the crystallites. The bonding between the two would thus be of a secondary valence type (polar bonding) rather than of the primary valence type.

Location of Amorphous and Crystalline Material. In native fibers it is possible to locate partially the amorphous and crystalline material with reference to the morphological structure. The morphological structure of most native cellulose fibers, such as cotton, consists of a thin outer limiting membrane or primary wall and a thicker secondary wall. The primary wall is thought to consist largely of noncellulosic constituents which contribute to part of the amorphous x-ray diagram. The major part of the crystalline cellulose exists in the secondary wall which is built up of fibrils aligned side by side to form layers or lamellae which may be observed in swollen cross sections of the fiber. These fibrils appear to be discrete entities as evidenced by the fact that they may be observed in the cytoplasm of young fibers. Furthermore, they can be separated from young fibers by mechanical treatment[63] and from mature fibers by the action of the papermaker's beater.[71] The structure of fibrils probably involves two regions, surface and internal.[72] The surface contains noncellulosic constituents as evidenced by their coloration with ruthenium red stain[62] while the interior contains pure cellulose.

Comparative x-ray and microscopic studies[73] indicate that in cotton fibers the crystalline pattern of cellulose arises from the fibril, and, as pointed out before, there is reason to believe that the amorphous x-ray pattern may be partly accounted for by the non-doubly refractive material which may be observed on the surface and between the birefringent fibrils. This assumption is based largely upon purification studies of young cotton fibers[74, 75] and upon orientation studies which will be discussed later.

Although crystalline cellulose appears to be associated with the fibril, it is not possible, however, to identify crystalline and amorphous cellulose in terms of other common cellulose classifications, such as alpha-, beta-, and

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[71] A. J. Bailey and R. M. Brown, *Ind. Eng. Chem.*, **32**, 57 (1940).
[72] R. F. Nickerson, *Ind. Eng. Chem.*, **32**, 1454 (1940).
[73] W. A. Sisson, unpublished results.
[74] W. A. Sisson, *Contrib. Boyce Thompson Inst.*, **8**, 389 (1937).
[75] W. A. Sisson, *Contrib. Boyce Thompson Inst.*, **9**, 239 (1938).

gamma-cellulose or in terms of degradation products such as hydrocellulose or oxycellulose. X-ray diagrams do show that beta- and gamma-cellulose (also hemicellulose) contain a larger percentage of amorphous material than does alpha, but at the same time they usually show appreciable quantities of crystalline cellulose. Likewise, it is not possible to correlate crystalline cellulose in terms of degree of polymerization (D.P.) since cellulose can be degraded to a very low D.P. without destroying the crystallinity; on the contrary the sharpness of the crystalline pattern usually increases with chemical degradation.

Formation of Crystalline Cellulose. Regarding the formation of crystalline cellulose in growing fibers, considerable knowledge has been obtained during recent years. Earlier workers[53] considered crystalline cellulose to be formed by a polymerization of glucose units at the inner surface of the cell wall. The long cellulose chains were considered to be built up and oriented with reference to each other (crystalline structure) and with reference to the fiber axis simultaneously with their formation. The work of Farr and Eckerson[62] and subsequent work by Farr,[63, 76, 77, 78] however, indicate that cellulose is first formed as particles within the cytoplasts in a manner similar to the formation of starch in the chloroplasts. These cytoplasts, which are present in the living protoplasm, later rupture, liberating the cellulose particles which then orient themselves end to end to form fibrils which in turn build up the fiber cell wall.

The first x-ray work on growing cotton fibers[79] was erroneously interpreted to indicate that the cellulose deposited in the young fiber was crystallographically different from that occurring in the mature fiber. It was later shown by Hess and coworkers[80, 81] that the x-ray pattern of young cotton fibers consists of two crystalline constituents and that the apparent change in crystal structure with growth was due to the pattern of the *Primärsubstanz* being displaced by that of cellulose as the fiber cell wall thickens. They found no x-ray evidence of crystalline cellulose below an age of 36 days. Later work[74] indicates that the cellulose pattern is not present in the x-ray diagram of young untreated cotton fibers because it is masked by a crystalline wax pattern (Hess's *Primärsubstanz*) which may be removed by extraction with organic solvents, and also by an amorphous

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[76] W. K. Farr, *J. Applied Phys.*, **8**, 228 (1937).
[77] W. K. Farr, *Contrib. Boyce Thompson Inst.*, **10**, 71 (1938).
[78] W. K. Farr, *Contrib. Boyce Thompson Inst.*, **12**, 181 (1941).
[79] G. L. Clark, L. W. Pickett, and W. K. Farr, *Science*, **71**, 293 (1930).
[80] K. Hess, C. Trogus, and W. Wergin, *Planta*, **25**, 419 (1936).
[81] W. Wergin, *Angew. Chem.*, **49**, 843 (1936).

diagram, which is removed by treatment with dilute alkali and bleaching. There is also evidence that the cellulose first formed may escape x-ray detection because it is in a highly swollen or hydrated state, as indicated by the fact that crystallization may be prohibited by extracting in nonpolar solvents or it may be facilitated by boiling in water. In purified fibers, crystalline cellulose may be identified as early as the fifth day, and the x-ray diagram shows that cellulose, after it is once formed, does not undergo a crystalline modification during fiber growth.

Regenerated Fibers. In native fibers, cellulose is formed in the cytoplasm under conditions favorable for crystal growth, and as a result cellulose of a high degree of crystallinity is often formed. According to the cellulose particle theory, the crystallites in native fibers are comparatively large with single cellulose chains apparently running the entire length of a single crystallite. In rayon fibers, however, the situation is quite different. When a viscose solution is made by mercerizing and xanthating native cellulose, the crystallinity of the original fiber is disrupted, and when the cellulose is regenerated a new crystallization must take place. This recrystallization consists first of a coagulation followed by a regeneration. Since these procedures usually take place simultaneously in a comparatively short time from a concentrated solution, the degree of crystallinity in regenerated cellulose is never as great as that of native cellulose. Furthermore, according to the network micellar theory the crystalline areas are comparatively small with a single cellulose chain occupying two or more crystalline areas which are separated by amorphous regions.

The available data indicate that in a rayon fiber the cellulose chains in the amorphous region do not lie in an entirely unoriented condition, but are partially oriented parallel to the fiber axis, the amount depending on the degree of stretching to which the fiber has been subjected. These oriented chains, however, fail to give definite diffraction lines because they do not have a three-dimensional orientation, which is the criterion of a crystalline substance. As pointed out by Mark,[46] the cellulose chains within a crystalline area may be compared to a bundle of parallel pencils, and those within the amorphous regions to a bundle of twigs. In the former case they fit perfectly together, while in the latter case they give a bundle containing many irregular spaces. The increased strength and decreased elongation of an oriented rayon and its improved water resistance may be due partly to a shifting of a large number of amorphous cellulose chains, which are easily swollen and deformed, toward the more rigid crystalline state where they are more strongly bound by polar forces and hydrogen bonds. Strength and elasticity are thus associated with crystalline cellulose; reactivity and ex-

tensibility with the amorphous portions. For example, the x-ray diagram shows that water does not enter into the crystalline areas, but in the amorphous areas water penetrates between the chains splitting interchain hydrogen bonding in forming its own bonds with cellulose hydroxyls and exerting a swelling action. In this way the wet tensile strength of rayon is reduced to a value considerably below the dry strength.

In general one may think of the cellulose molecule as having two different tendencies; (1) the tendency to fraternize or to crystallize under the influence of mutual secondary valence forces between the chains, and (2) the tendency to be independent of its neighbors and to exist at random owing to the kinetic energy of the molecule. It is probable that stretching would assist the former forces, and it has been observed by several workers[46] that mechanical and chemical treatments may change the relative amounts of the crystalline and amorphous parts in a rayon fiber. This effect appears more pronounced in cellulose derivatives than in cellulose itself, apparently due to the fact that the forces between the cellulose chains have been reduced by esterification of the hydroxyl groups.

Cellulose Derivatives. The crystallinity of native and regenerated fibers is little affected by heat after crystallization has once taken place. Certain derivatives, however, such as cellulose triacetate and cellulose tributyrate, may be solidified from the molten state to produce either an amorphous or a crystalline structure, depending upon the temperature gradient.[82] For example, if these esters are solidified from their melts under a temperature gradient corresponding to only a few degrees below the melting point, highly crystalline solids are produced. If they are quenched at temperatures of approximately 200°C. below their fusion point then the liquid disordered array is largely preserved. Quenching apparently does not leave the chains in a disordered array in the sense that liquid benzene is amorphous; instead it apparently leaves chain sections which are locally parallel but randomly rotated around their long axis. X-ray diffraction patterns show that if these randomly rotated chains are heated at a much lower temperature than the softening point, they acquire sufficient kinetic energy to rearrange themselves into the stable lattice array.[82] The effect of quenching and annealing on the crystallinity is illustrated in Figure 7.

The action of heat in rearranging the "frozen in" amorphous structure of quenched derivatives indicates a high degree of mobility in the solid state of the cellulose ester units, or chain segments, when they are internally plasticized by the ester groups. Cellulose itself does not show a similar

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[82] W. O. Baker, C. S. Fuller, and N. R. Pape, *J. Am. Chem. Soc.*, **64**, 776 (1942).

phenomenon toward heat alone, apparently due to hydrogen bonds. This is supported by the fact that if the derivatives contain unsubstituted hydroxyl groups, which are capable of forming hydrogen bonds, then the crystallinity cannot be improved by heating.[82] It should be noted in this case that the inherent tendency for crystallization is much less in the case of the

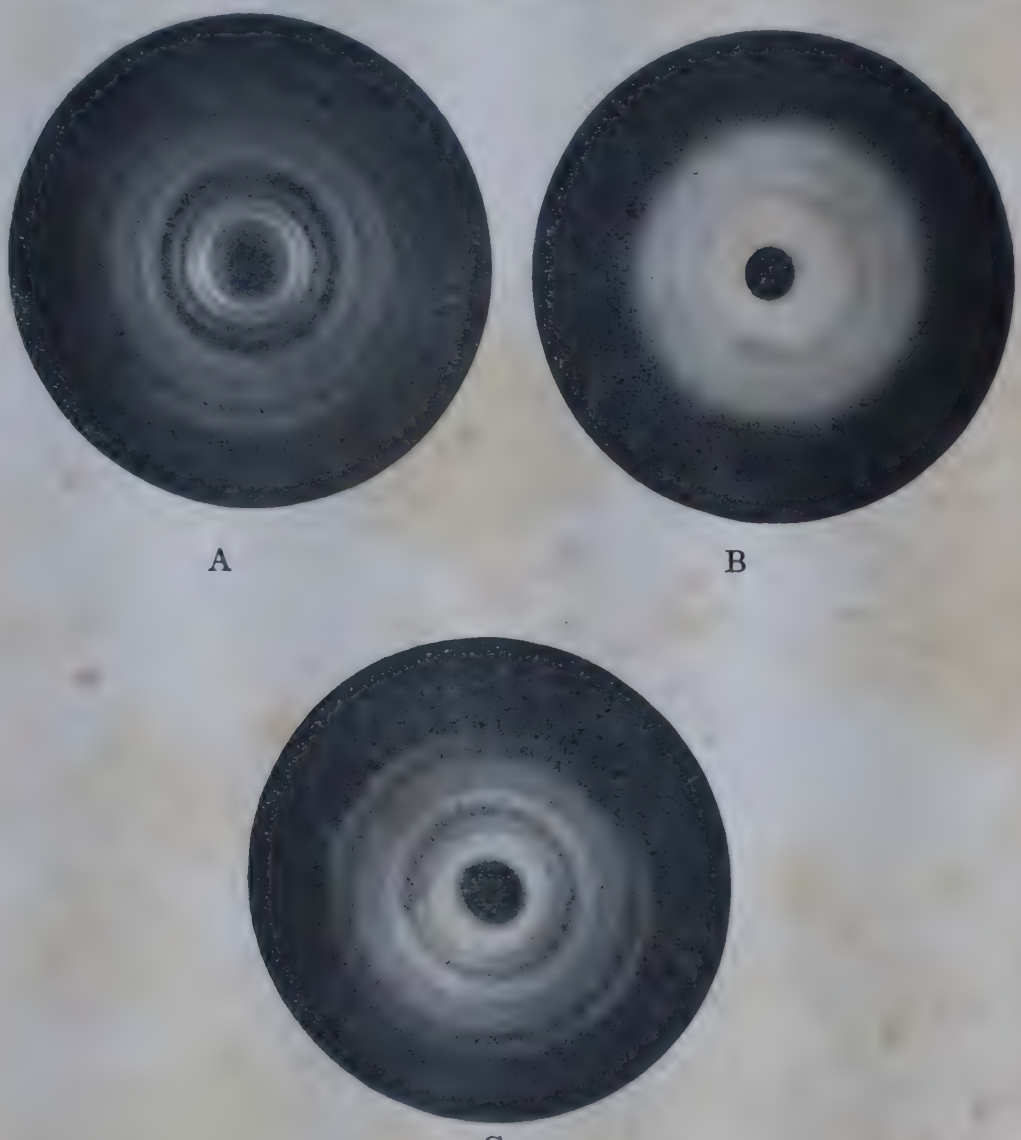

FIG. 7.—X-RAY PATTERNS OF CELLULOSE TRIACETATE SHOWING EFFECT OF HEAT-TREATMENT (BAKER, FULLER, AND PAPE[82]).

(A) Solidified near melting point; (B) quenched at −75°C.; (C) is (B) annealed 2 hours at 225°C.

partially substituted derivatives. The attraction between chains is less than in the case of the fully substituted chains (see Chapter IX, Section A on "Solubility") and, in addition, difficulty of crystallization may be attributed to the lack of order in the chains due to the random arrangement of the hydroxyl groups (see p. 253). Here, as is the case with cellulose, the heating must be supplemented by a solvent or swelling agent such

as water which splits the interchain hydrogen bonding and forms its own bonds with the cellulose hydroxyls.

The importance of polar solvents is further emphasized by the work of Spence[83] who has noted that polar solvents like ethylene chlorohydrin give cellulose triacetate films which are more brittle and more crystalline than do less polar solvents like chloroform. Likewise, an indefinite or amorphous pattern is obtained when cellulose acetate is deacetylated in a non-aqueous medium such as an ethanol-sodium hydroxide solution. The amorphous pattern is changed to a well-defined crystalline cellulose hydrate pattern when the sample is heated with water. In a recrystallized sample, the crystallites may or may not be oriented with respect to a common axis depending upon whether or not the fiber is stretched.

The ratio of crystalline to amorphous cellulose is thought to have considerable influence upon physical properties. For example, Jones and Miles[84] have proposed that amorphous constituents confer flexibility in films, while Sheppard and Newsome[85] have suggested that small crystallites produce flexibility. According to Mark,[46] the physical properties—tenacity, elasticity, etc.—are functionally related to the amount of crystalline material, while the reactivity of the fiber—swelling, drying, ease of chemical reactions, etc.—is to be associated with the amorphous parts. The crystallized portions of the material may be regarded as the reinforcing backbone of the structure, while the unordered regions may be regarded as the weak spots.

The proper interpretation of an amorphous x-ray diagram is often difficult. For example, it might be due to chains having a completely random orientation, to parallel chains which have random rotation around their own axis, or to chains whose crystalline regularity has been disturbed by substituted side groups. For example, most of the lower-substituted cellulose derivatives give the amorphous pattern and only in special cases, such as the quenching discussed earlier, are the final trisubstitution products known to be amorphous. One explanation for the amorphous pattern of a lower derivative may be the presence of a higher degree of substitution on the surface of the crystallite, which, owing to the expansion of the lattice, may be an obstacle to perfect crystallization.[86] A more logical explanation would appear to lie in the heterogeneous distribution of the substituted groups along the cellulose chain. The distribution varies in neigh-

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[83] J. Spence, *J. Phys. Chem.*, **45**, 401 (1941).
[84] G. G. Jones and F. D. Miles, *J. Soc. Chem. Ind.*, **52**, 251T (1933).
[85] S. E. Sheppard and P. T. Newsome, *J. Soc. Chem. Ind.*, **56**, 256T (1937).
[86] G. Centola, *Gazz. chim. ital.*, **65**, 1230 (1935).

ring chains and in different sections of the same micelle, and regularity distribution of the groups along the chain is obtained only when the tri-stituted product is approached.[87]

(*d*) *Orientation*

. the present discussion, the term orientation will refer to the arrange-it or alignment of cellulose crystallites with reference to the fiber axis, with reference to the fiber surface. The term refers only to crystallite

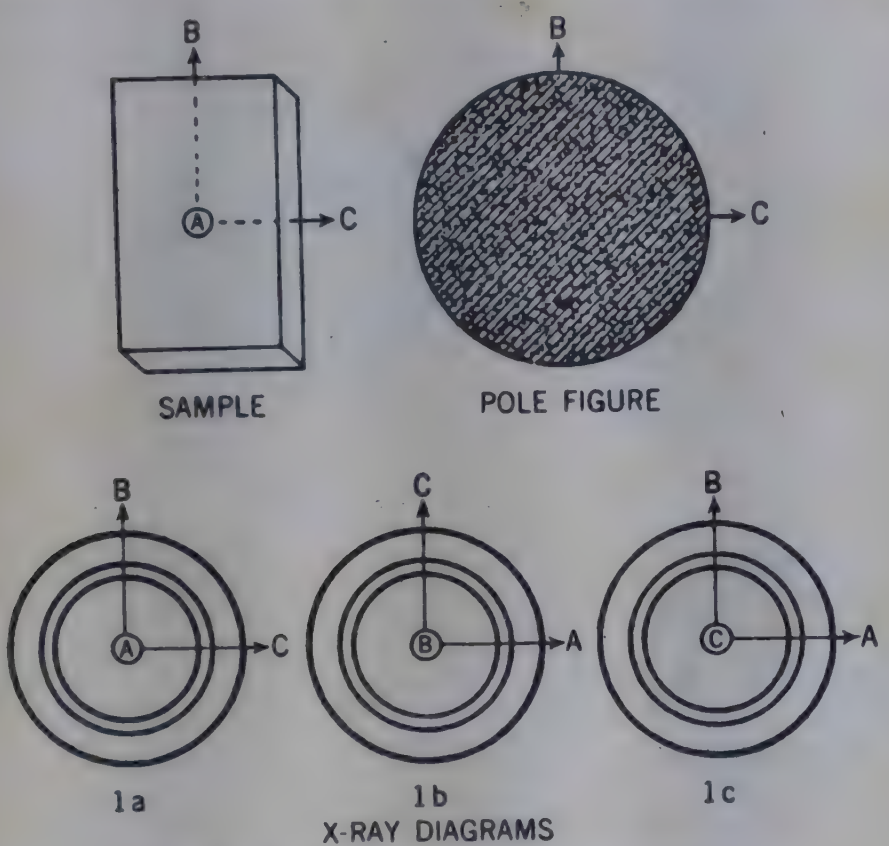


FIG. 8.—RANDOM ORIENTATION (SISSON[88]).

The same x-ray diagram is obtained with the sample at any angle to the x-ray beam.

or micellar orientation, and unless otherwise noted it has no reference to the arrangement or orientation of the individual molecules within the crystallite (crystalline structure). It is thus theoretically possible to have an amorphous fiber with parallel orientation or a crystalline fiber with a random orientation, and the orientation of a fiber can be changed without appreciably affecting the crystallinity, or vice versa. A highly oriented fiber may be considered as more crystalline only in the sense that the fiber

[87] M. Mathieu, *Trans. Faraday Soc.*, **29**, 122 (1933).
[88] W. A. Sisson, *J. Phys. Chem.*, **40**, 343 (1936).

as a whole possesses greater crystallinity in one direction. As previously pointed out, the degree of crystallinity is estimated from the sharpness of the diffraction rings, while orientation is measured by the concentration of the rings into arcs.

Types and Measurement of Orientation. The general term *orientation*, as used in the literature, usually refers to the alignment of the *b* axes of the crystallites with reference to the fiber axis, but it is possible to have other types which may be classified as follows.[88]

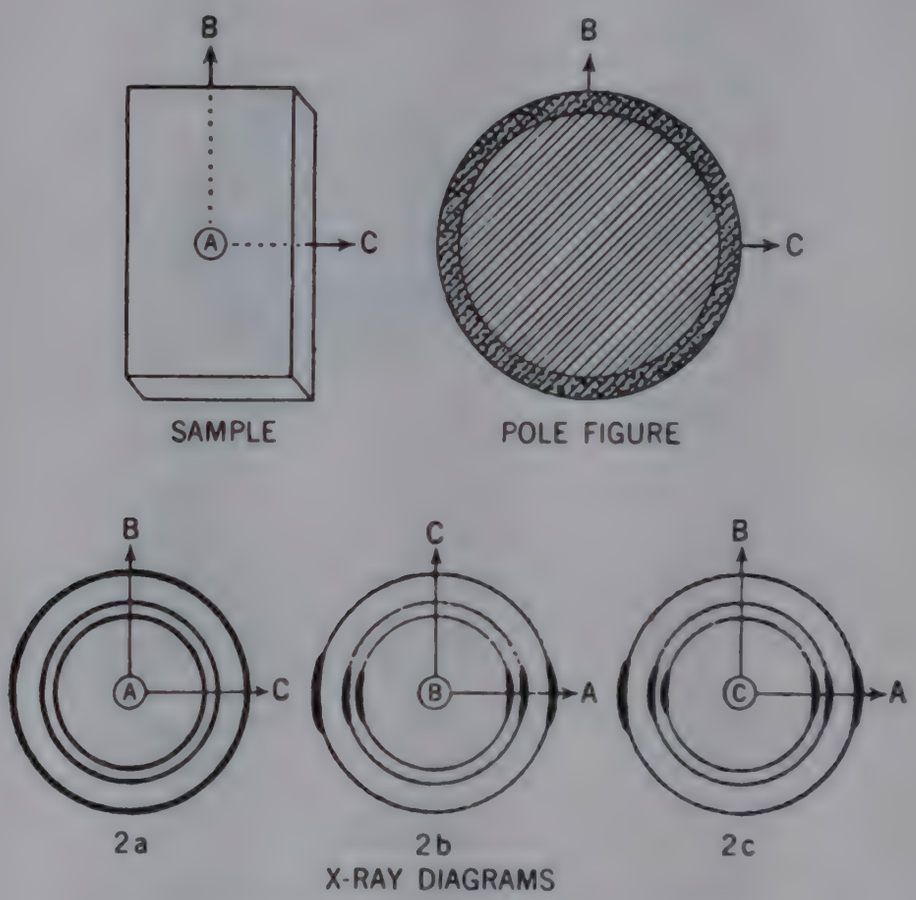


FIG. 9.—UNIPLANAR ORIENTATION (SISSON[88]).

With the *a* axis parallel to the x-ray beam, the diagram is random with all lines present; with the *b* or *c* axis parallel, a fiber pattern is obtained with all lines present.

Random Orientation. The crystallites are arranged in all possible directions (see Fig. 8).

Uniplanar Orientation. The only limitation imposed is that the *b* axes (direction of cellulose chains) of the crystallites lie parallel to a plane. The crystallites lie at random in the plane and have all possible rotations around their *b* axes (see Fig. 9).

Selective Uniplanar Orientation. The orientation is similar to a uniplanar

orientation in that the *b* axes are parallel to and are arranged at random in a plane, but differs in that the (101) planes of the crystallite have a selective orientation parallel to a plane which is usually the large surface of the specimen (see Fig. 10).

Uniaxial Orientation. The only limitation imposed is that the *b* axes of the crystallite have a preferred orientation parallel to the fiber axis (see Fig. 11).

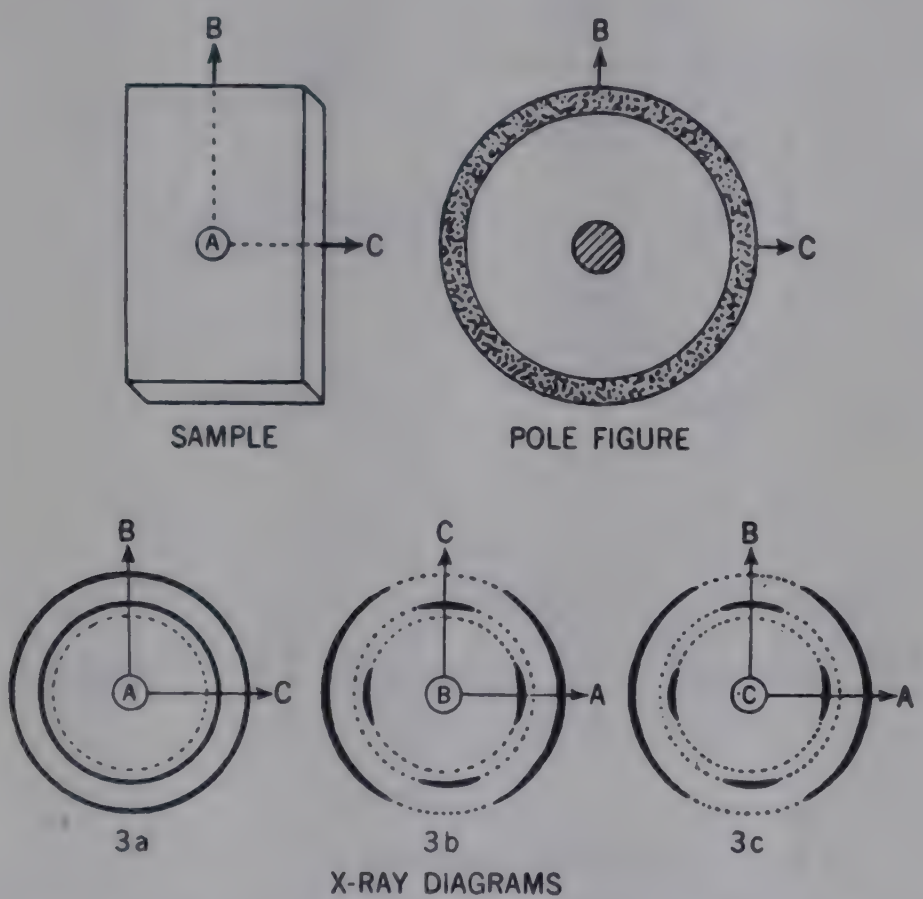


FIG. 10.—SELECTIVE UNIPLANAR ORIENTATION (SISSON[88]).

With the *a* axis parallel to the x-ray beam, a random oriented pattern is obtained with the 101 line missing and the $10\bar{1}$ present; with the *b* or *c* axis parallel, the 101 line is present as a dense arc on the equator, while the $10\bar{1}$ is present only as a faint arc on the meridian.

Selective Uniaxial Orientation. The *b* axes of the crystallites are not only parallel to the fiber axis, but the (101) planes are also parallel to a plane containing the fiber axis, a combination of a uniaxial orientation and a selective uniplanar orientation (see Fig. 12).

Stereographic projections, or pole figures, representing the various types of orientation and their corresponding x-ray diagrams for the native cellulose structure are illustrated diagrammatically in Figures 8, 9, 10, 11, and 12. In the pole figures the dotted areas represent the projection of the

b axes and the cross-hatched areas the projection of the (101) directions A, B, and C represent arbitrary reference axes within the sample.

Measurement of Orientation. The usual methods of determining orientation consist of a microscopic study in ordinary light of the visible fibrils, striations, and cracks; the study of extinction angles, of dichroism, and of other phenomena in polarized light; or the study of x-ray diagrams. If the orientation is random, the x-ray diffraction rings exist as continuous circles;

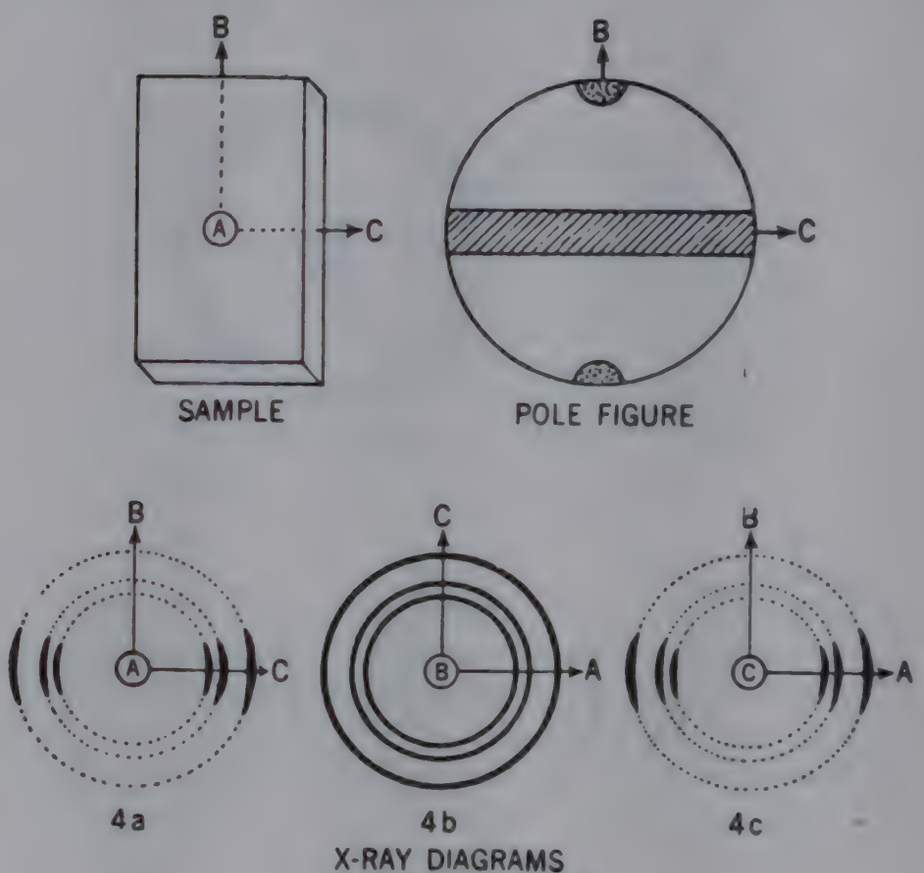


FIG. 11.—UNIAXIAL ORIENTATION (SISSON[88]).

With the *a* or *c* axis parallel to the x-ray beam, the 101, $10\bar{1}$, and 002 lines all exist as intensity maxima at the equator and their relative densities remain constant with rotation of the sample around the *b* axis (fiber axis). If the *b* axis is parallel to the x-ray beam, a random pattern is obtained.

if it is parallel, the rings are concentrated into arcs. The usual x-ray diagram represents the average orientation throughout a millimeter section of several hundred fibers, while microscopic results are specific for localized sections of single fibers. The principal value of the x-ray data, therefore, lies in the fact that it gives a general or average value, which can be estimated quantitatively.

A quantitative x-ray method for the estimation of orientation has been developed upon the assumption that the intensity of the 002 diffraction ring

t any angle to the equator is proportional to the number of crystallites in he fiber at the same angle to the fiber axis.[89] Intensity measurements are nade with a microdensitometer equipped with a rotating stage. Measure-nents are made through 360° around the 002 line (x-ray photograph made n a flat film) and the orientation expressed by percentage distribution

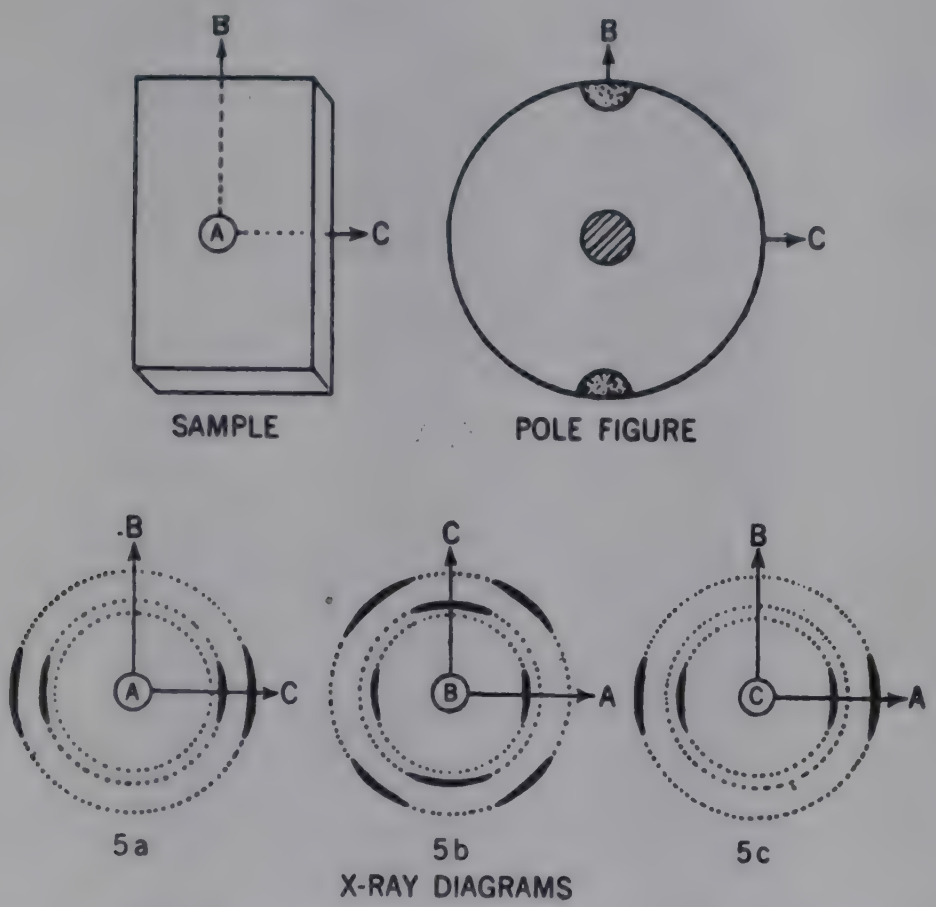


FIG. 12.—SELECTIVE UNIAXIAL ORIENTATION (SISSON[88]).

With the *a* axis parallel to the x-ray beam, the 101 line is missing but the $10\bar{1}$ and 002 exist as intensity maxima at the equator; with the *c* axis parallel, the 101 is missing and the 101 and 002 present as intensity maxima at the equator; with the *b* axis parallel, the 101 is present at the equator, the $10\bar{1}$ at the meridian, and the 002 as four arcs.

curves in which the relative intensity is plotted against the angle to fiber axis. Typical distribution curves are shown in Figure 13.

Native Fibers. The major axis of the unit cell is known to be oriented n most fibers either parallel or at some spiral angle to the fiber axis. Owing to the cylindrical form of cellulose fibers, however, it is difficult to detect a further orientation of the lattice with reference to the cell wall (uniplanar selective orientation). Likewise, it is known that the

[89] W. A. Sisson and G. L. Clark, *Ind. Eng. Chem., Anal. Ed.*, **5**, 296 (1933).

crystallite orientation is related to the fibril orientation, but it is impossible to tell whether the fibril has a biaxial or a uniaxial orientation.

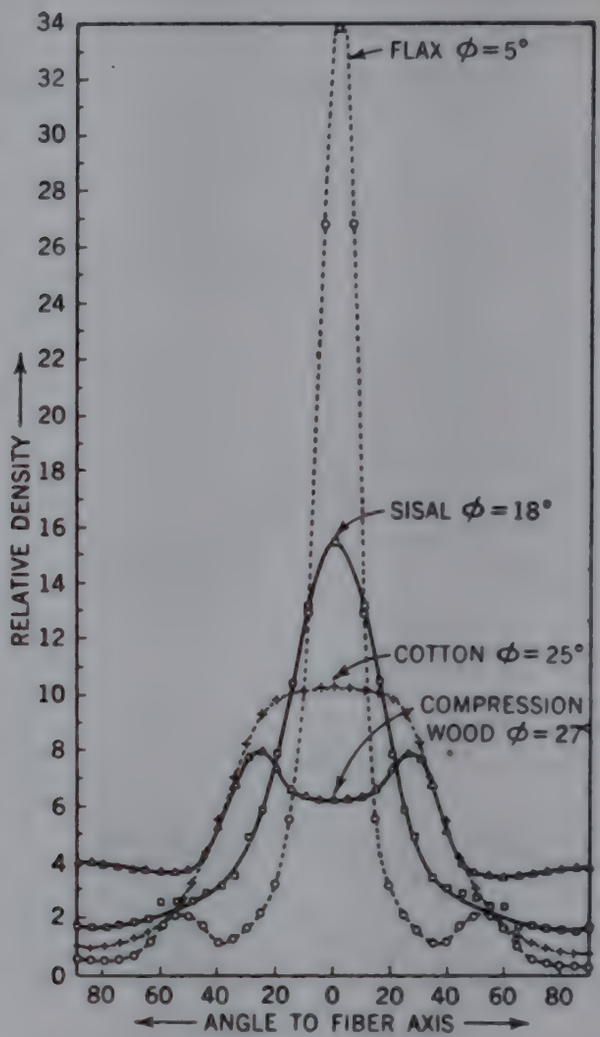


FIG. 13.—MEASURED DENSITY DISTRIBUTION CURVES AROUND THE 002 DIFFRACTION RING FOR SEVERAL NATURAL FIBERS (SISSON[90]).

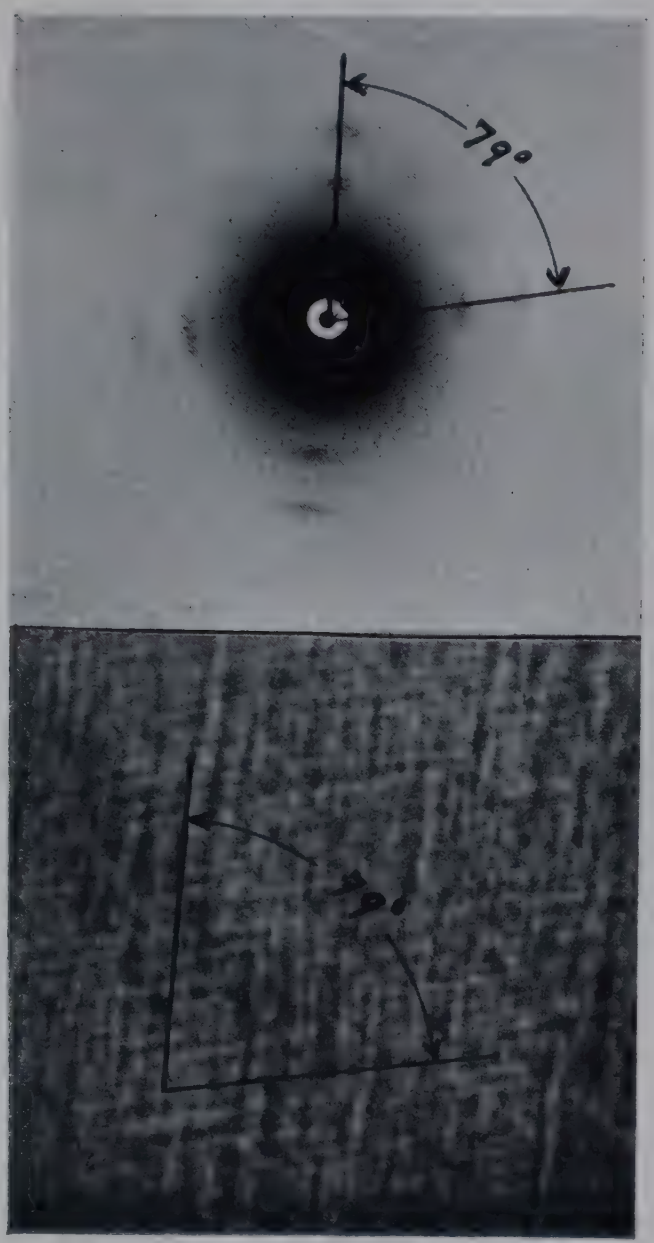
Relationship of Fibril to Crystallite Orientation. Sponsler[91] first pointed out that the difficulty of splitting longitudinally such a small cell as the cotton fiber and pressing it flat for x-ray analysis could easily be overcome in the large wall of the single-celled, marine alga, *Valonia ventricosa*, which often grows to a diameter of over 3 cm. By taking x-ray diagrams of flat pieces of the *Valonia* cell wall, Sponsler was able to show that the (101) planes lie roughly parallel to the surface of the cell wall (selective orientation). Later Astbury, Marwick, and Bernal[92] further showed that two principal sets of

[90] W. A. Sisson, *Ind. Eng. Chem.*, **27**, 51 (1935).

[91] O. L. Sponsler, *Protoplasma*, **12**, 241 (1931).

[92] W. T. Astbury, T. C. Marwick, and J. D. Bernal, *Proc. Roy. Soc.* (*London*), **B109**, 443 (1932).

crystallites crossed each other in the cell wall at an angle of approximately 80° (double biaxial orientation). Subsequent microscopic studies[66, 93] have shown that *Valonia* is built up of two sets of fibrils, crossing each other at an



A

B

FIG. 14.—X-RAY DIAGRAM AND PHOTOMICROGRAPH OF *Valonia* TAKEN PERPENDICULAR TO THE MEMBRANE SURFACE SHOWING DIRECTION OF CRYSTALLITE AND FIBRIL ORIENTATION (SISSON[66]).

angle of approximately 80°, as illustrated in Figure 14B. X-ray diagrams of the same sample show the usual equatorial diffraction lines concentrated into four arcs with the sets approximately 80° to each other, as shown in

[93] R. D. Preston and W. T. Astbury, *Proc. Roy. Soc. (London)*, **B122,** 76 (1937).

Figure 14A. The dispersion from a perfectly parallel crystallite orientation can be accounted for completely on the basis of the observed deviation of the fibril orientation. Thus by comparison of x-ray diagrams and photomicrographs of the same sample it has been shown that the *b* axes of the cellulose unit cells are oriented parallel to the axis of the fibrils. In a similar manner it has been shown that the fibril possesses a definite biaxial orientation.[66]

Further confirmation of the relationship of fibril structure to orientation

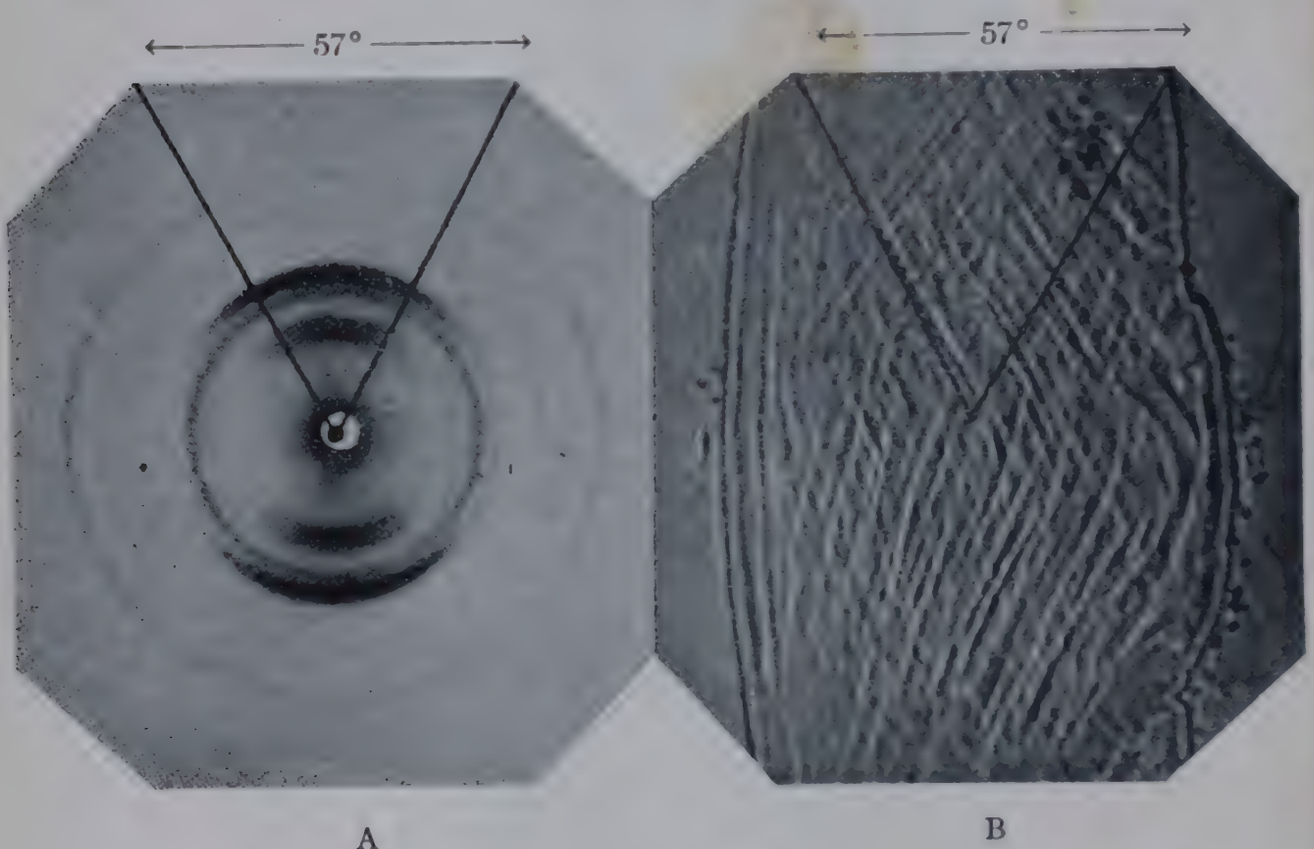


FIG. 15.—COMPARISON OF X-RAY AND FIBRIL ORIENTATION (SISSON[75])

(A) X-ray diffraction pattern of mature cotton; (B) photomicrograph of cotton fiber slightly swollen in phosphoric acid to bring out fibril structure.

comes from the fact that fibrils may be scraped from the inner surface of a *Valonia* cell and dried to form a film, or stretched to form a fiber.[66] In every fiber so far examined, it has been possible to account completely for the orientation observed in the x-ray diagram on the basis of the fibril orientation observed in the microscope.[73] For example, the high degree of fibering in the x-ray diagram of ramie fibers[90] and the rather wide deviation from a parallel orientation in cotton[75] may be directly correlated with the fibril orientation observed in the cell wall as illustrated in Figure 15.

Selective Orientation. In native fibers the question naturally arises as to

whether or not the *a* or *c* axis of the crystallites has a selective orientation with reference to the cell wall similar to that found in *Valonia*. It has been shown theoretically[90] that if the (101) plane is oriented parallel to the fiber surface, then, as the spiral angle ϕ of the fibrils with reference to the fiber axis becomes larger, the two 101 diffraction arcs remain at the equator, while the 002 and $10\bar{1}$ arcs each split into four arcs which move nearer the meridian, as illustrated in Figure 16. If the fibrils, however, are rotated at

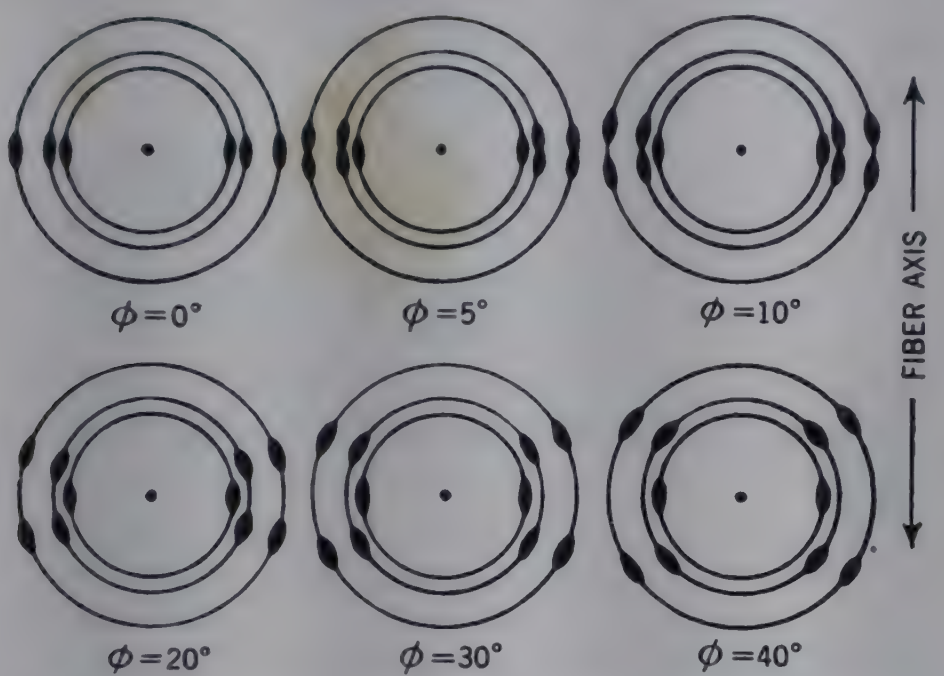


FIG 16.—THEORETICAL X-RAY PATTERNS FOR CELLULOSE FIBERS SHOWING EFFECT OF SELECTIVE ORIENTATION AT VARIOUS SPIRAL ANGLES (SISSON[90]).

random around their own axis or have a twist, then, as the spiral angle ϕ becomes large, all of the equatorial arcs divide and move toward the meridian, as illustrated in Figure 17. All cellulose fibers possessing a large spiral angle give x-ray diagrams typical of Figure 17, indicating the absence of selective orientation.

Spiral Orientation. In a native fiber possessing a spiral structure, the x-ray diagram does not represent the true orientation. With the x-ray beam perpendicular to the fiber axis, the x-ray pattern pictures the three-dimensional orientation of the crystallites projected on a plane. Thus the density distribution around the x-ray diffraction ring is always shifted toward the equator because of the cylindrical form of the fibers; the fibrils in that portion of the cell wall parallel to the x-ray beam diffract on the equator rather than at an angle corresponding to the spiral angle. Preston[94] has pointed

[94] R. D. Preston, *Trans. Faraday Soc.*, **29**, 73 (1933).

out that the same factor causes anomalous values when the orientation is measured by the refractive index method.

The type of x-ray intensity distribution curves to be expected from a series of well-oriented spiral structures, neglecting the edge effect, is shown in Figure 18. These curves show: (1) the total distribution curve (upper dotted line) is a function of both the spiral angle ϕ and the distribution about this angle; (2) the x-ray pattern may not indicate a spiral structure although one is present; (3) in order to obtain an x-ray pattern showing four intensity maxima, the spiral angle must be large and the deviation from the spiral angle small; and (4) the maxima of the x-ray density curve may not necessarily correspond to the correct spiral angle. The measured density distribution curves for four natural fibers are shown in Figure 13. These curves show that cotton and compression wood have about the same average spiral angle but that the deviation from this angle is greater in the case of cotton.

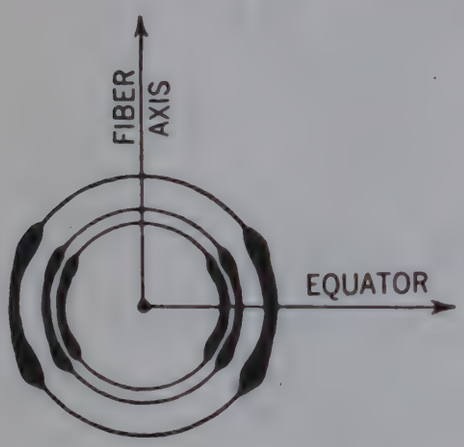


FIG. 17.—THEORETICAL X-RAY PATTERN FOR A CELLULOSE FIBER SHOWING THE EFFECT OF NONSELECTIVE ORIENTATION AT A LARGE SPIRAL ANGLE (SISSON[90]).

Formation of Orientation during Fiber Growth. Most of the x-ray work regarding the orientation of the cellulose crystallites during fiber growth has been carried out on cotton and wood fibers. In the first x-ray examination of young cotton fibers,[79] evidence of cellulose orientation was not found below the 35-day sample. Subsequent work[75] on purified fibers has shown that, in general, fibers younger than about 25 days give the pattern of randomly oriented cellulose; between approximately 25 and 35 days there develops a preferred orientation which does not change appreciably with further wall thickening.[95] In young wood cells the cellulose x-ray pattern becomes oriented after about the tenth day.[96] In *Valonia* there can be detected in the youngest cells an orientation which does not change with further cell enlargement.[66]

Little is known regarding the fundamental reason why orientation is produced in a growing fiber. Herzog has suggested[97] that it is due to tension during growth and he supported his suggestion by showing that preferred orientation is more pronounced in viscose fibers if tension is applied during

[95] E. E. Berkley, *Textile Research*, **9**, 355 (1939).
[96] G. J. Ritter and C. W. Stillwell, *Paper Trade J.*, **98**, 37 (May 31, 1934).
[97] R. O. Herzog, *Ber.*, **58B**, 1254 (1925).

the spinning process. Cytoplasmic material scraped from the inner surface of a *Valonia* cell[66] and dried in the form of a fiber shows that the crystalline cellulose present in the cytoplasm can be oriented by the application of tension during drying.

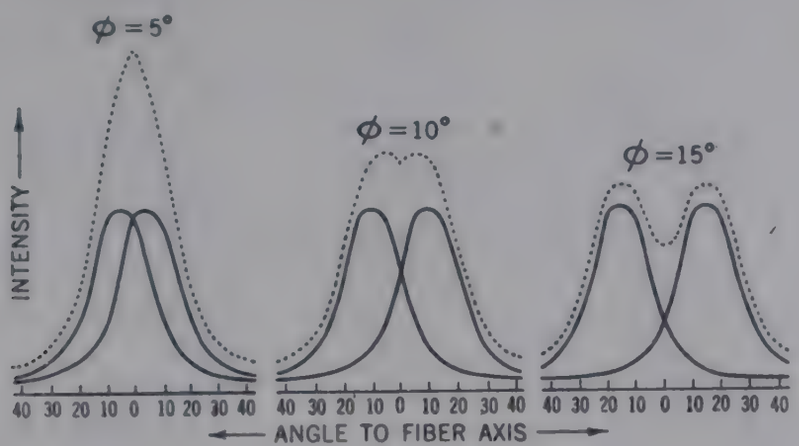


FIG. 18.—THEORETICAL DENSITY DISTRIBUTION CURVES FOR FIBERS HAVING VARIOUS ANGLES OF SPIRAL ORIENTATION (SISSON[90]).

Relationship of Orientation to Physical Properties. The influence of orientation upon the physical and chemical properties of cellulose has been discussed by many investigators, particularly with reference to the degree of mercerization, tensile strengths, classification, elasticity, and dyeing properties of cotton[98–102] and the density, tensile strength, expansion, and shrinkage of wood.[103, 104, 105] As the orientation increases, the luster increases, depth of dyeing decreases, fibers swell more in diameter and shrink more in length, the tensile strength increases, and the elongation decreases.

In ramie the cellulose crystallites have an orientation almost parallel to the fiber axis. As a result, ramie fibers have the greatest tensile strength of all natural fibers, but they are brittle and weave into a relatively harsh fabric. Perfect alignment thus makes for great strength and rigidity in the fiber direction but brittleness in the transverse direction. In cotton the crystallites are inclined at an angle to the fiber axis; thus cotton does not

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[98] G. L. Clark, *Ind. Eng. Chem.*, **22,** 474 (1930).
[99] H. Mark, *J. Soc. Dyers Colourists,* **48,** 53 (1932).
[100] W. Schramek, *Z. physik. Chem.*, **B13,** 462 (1931).
[101] W. A. Sisson, *Textile Research,* **7,** 425 (1937).
[102] C. M. Conrad and E. E. Berkley, *Textile Research,* **8,** 341 (1938).
[103] D. B. Anderson, *Ohio J. Sci.*, **28,** 299 (1928).
[104] A. Koehler, *Trans. Am. Soc. Mech. Engrs.*, **53,** No. 2, Wood Industries, 17 (1931).
[105] K. Lark-Horovitz and W. I. Caldwell, *Nature,* **134,** 23 (1934).

have the tensile strength of ramie, but it is a more resilient fiber and weaves into a softer fabric.

By using a quantitative x-ray method for comparing orientation it is possible to obtain a close correlation between orientation and tensile strength of raw cotton as shown in Table 1. The general usefulness of the

TABLE 1

RELATIONSHIP OF COTTON STRENGTH TO X-RAY ORIENTATION (SISSON[101])

Strength, lbs./sq. in.	X-ray angle, degrees	Strength, lbs./sq. in.	X-ray angle, degrees
111,900	24.2	84,000	38.5
105,000	23.2	82,700	37.3
92,200	30.5	80,000	37.5
92,000	34.1	72,900	42.6
84,400	35.6	71,900	43.0

method, however, is limited by the fact that it does not indicate some types of degradation (tendering) which decrease fiber strengths substantially.[102]

In wood fibers there is a great variation in orientation depending upon the species of wood, the season, and the position of growth.[106] Woods which have a parallel orientation of the crystallites are those which split easily, have high tensile strength, and undergo little longitudinal shrinkage. When the orientation is more random, the wood is tougher but the tensile strength is lower and the shrinkage high.

Regenerated Fibers. The usual method of producing orientation in a regenerated fiber is by stretching. This produces an alignment of the major crystallographic axis parallel to the direction of stretching. The cellulose crystallite also possesses a secondary or minor orienting tendency, as shown by the fact that a minor axis [101] of the crystallite is oriented parallel to the direction of shrinkage when swollen cellulose is dehydrated.[107] Since shrinkage always occurs during the formation of a regenerated fiber, it is necessary to consider the orientation of both the (101) plane and the *b* axis of the crystallite as affected by dehydration and by stretching.

In regenerated fibers the various types of orientation (random, uniplanar, selective uniplanar, uniaxial, and biaxial) will be used as previously defined for native fibers. These types will be illustrated by drawings of the unit

[106] C. W. Stillwell, *Crystal Chemistry*. McGraw-Hill, New York, 1938.

[107] W. A. Sisson, *J. Phys. Chem.*, **44**, 513 (1940).

cell arrangement and the corresponding x-ray diagram as shown in Figure 19. The orientation of the unit cell is located by the *b* axis (direction of cellulose chain) and the (101) plane which is shaded in the drawing.

Shrinkage. Regenerated cellulose, when first formed, is usually in a highly swollen condition. Upon dehydration, produced either by chemical reagents or by drying, considerable shrinkage in volume takes place, and, simultaneously with this shrinkage, orientation is produced. The type of orientation is apparently governed by the direction of shrinkage, and the degree of orientation by the degree or percentage of that shrinkage. The x-ray results on shrinkage are summarized in Figure 20.

If a swollen cube of cellulose shrinks along one axis (Fig. 20AE), the (101) planes are oriented perpendicular to the direction of shrinkage, but

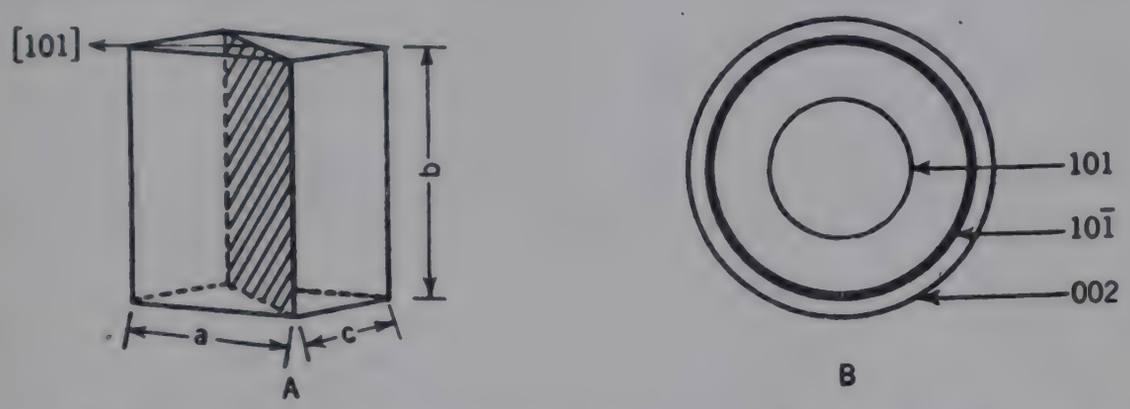


FIG. 19.—UNIT CELL ARRANGEMENT AND X-RAY DIAGRAM OF HYDRATE CELLULOSE (SISSON[107]).

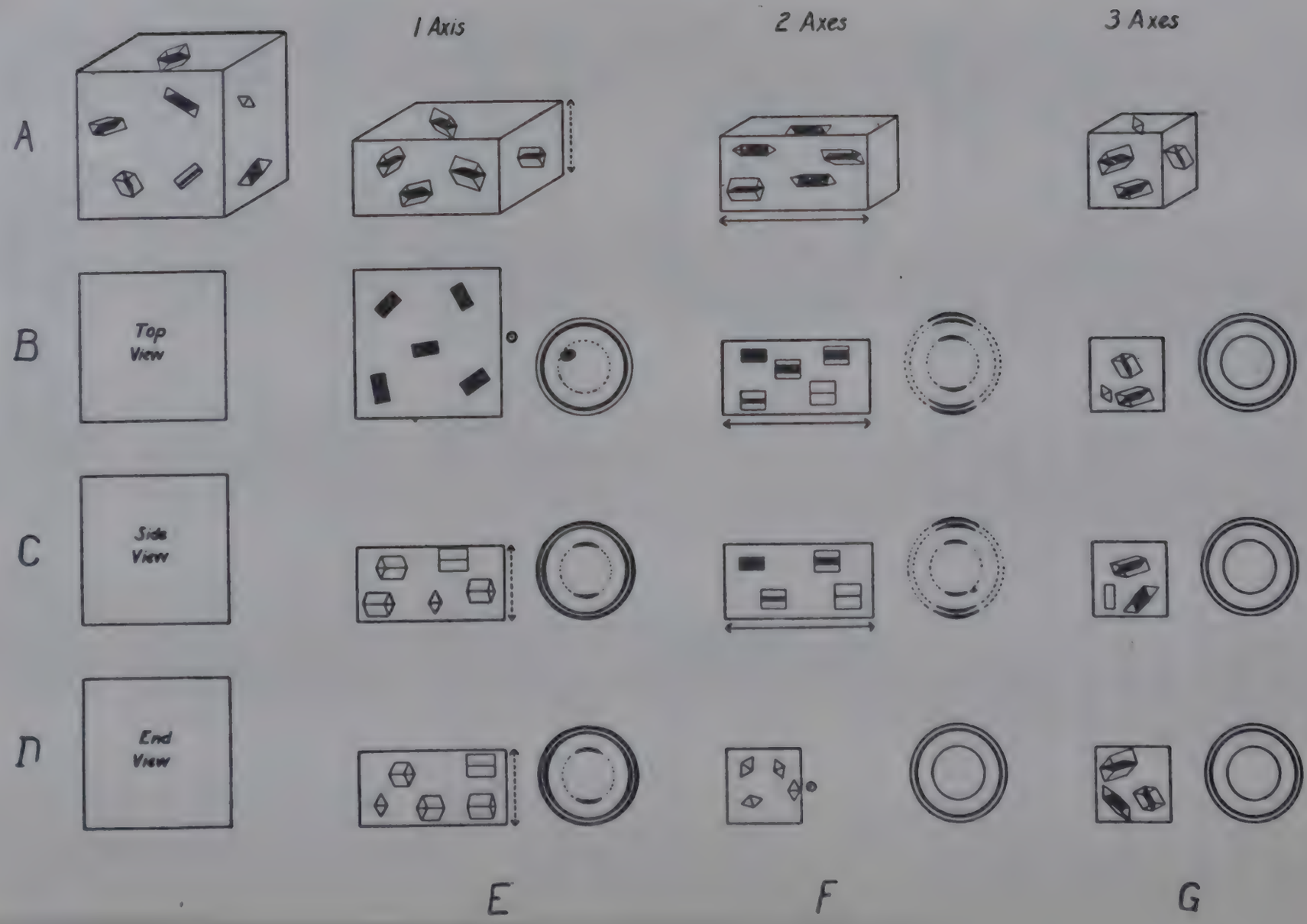
(A) Schematic representation of unit cell showing location of unit cell axis and the (101) plane, which is shaded; (B) x-ray diagram of hydrate cellulose showing location of 101, 10$\bar{1}$, and 002 diffraction rings.

there is random arrangement of the *b* axes about this direction. This type of orientation resulting from shrinkage along one axis may be classified as a selective uniplanar orientation.

If shrinkage takes place in two directions (Fig. 20AF), the *b* axes of the unit cells are oriented parallel to the axis which did not shrink, but the unit cells have random orientation around their *b* axes. This type of orientation resulting from shrinkage along two axes may be classified as a uniaxial orientation.

If shrinkage takes place in all directions (Fig. 20AG), the unit cells have a random orientation when viewed from any direction.

Deformation. Another property of swollen coagulated cellulose is that it can be deformed, either by tension or pressure, to produce preferred orientation. The results obtained by elongation and contraction are graphically



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represented in Figure 21 in the same manner as the results on shrinkage in Figure 20.

The results obtained by either shrinkage or elongation may be summarized as follows: a random orientation is obtained in the swollen condition or by shrinkage along three axes; uniaxial orientation by shrinkage along two axes, or by elongation on one axis and shrinkage along two; uniplanar orientation by shrinkage along one axis, or by elongation on two axes and shrinkage along one; and biaxial orientation by shrinkage along one axis and elongation along one axis.

It is difficult to evaluate separately the effect of shrinkage and deformation, since the two always act collectively in producing a dry sample necessary for x-ray diffraction analysis. The most tangible factor which may be correlated with the production of orientation appears to be the relative change in sample dimensions. In terms of dimensional changes, the following general conclusions may be drawn: whenever there is a relative increase in dimension of a sample in one direction, the *b* axes of the unit cell tend to orient parallel to that direction; if there is a relative decrease in dimension in one direction, the (101) planes are oriented perpendicular to that direction. The degree of orientation in each case is proportional to the relative change in dimensions of the sample. After a given type of orientation is formed, it is possible in some instances to change from one type to another. For example, if a uniplanar sample is stretched (perpendicular to fiber axis), it is first changed into an imperfect biaxial and eventually into a uniaxial orientation. If uniaxial or biaxial oriented samples are pressed (perpendicular to fiber axis), they are changed into a uniplanar orientation.

Rayons. In the industrial production of rayons, deformation is usually followed by or produced simultaneously with shrinkage; the two factors

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FIG. 20.—SCHEMATIC REPRESENTATION OF TYPES OF ORIENTATION AND CORRESPONDING X-RAY DIAGRAMS OBTAINED WHEN SWOLLEN HYDRATE CELLULOSE SHRINKS ALONG VARIOUS AXES (SISSON[107]).

A cube of swollen coagulated cellulose having random orientation is diagrammatically represented in the upper left-hand corner. The types of orientation obtained when the cube shrinks along different axes are represented diagrammatically in the vertical columns *E*, *F*, and *G*. The corresponding x-ray diagrams are shown with the sketches. The horizontal columns A, B, C, and D show the orientation and x-ray diagrams when viewed from different positions. Arrows indicate the direction of fiber axis; solid lines represent major axis (orientation of *b* axis of unit cell) while dotted lines represent minor axis (orientation of perpendicular to (101) plane of unit cell). Thus Figure 20BE, for example, refers to the orientation produced by shrinkage in one direction when viewed from the top (axis of shrinkage).

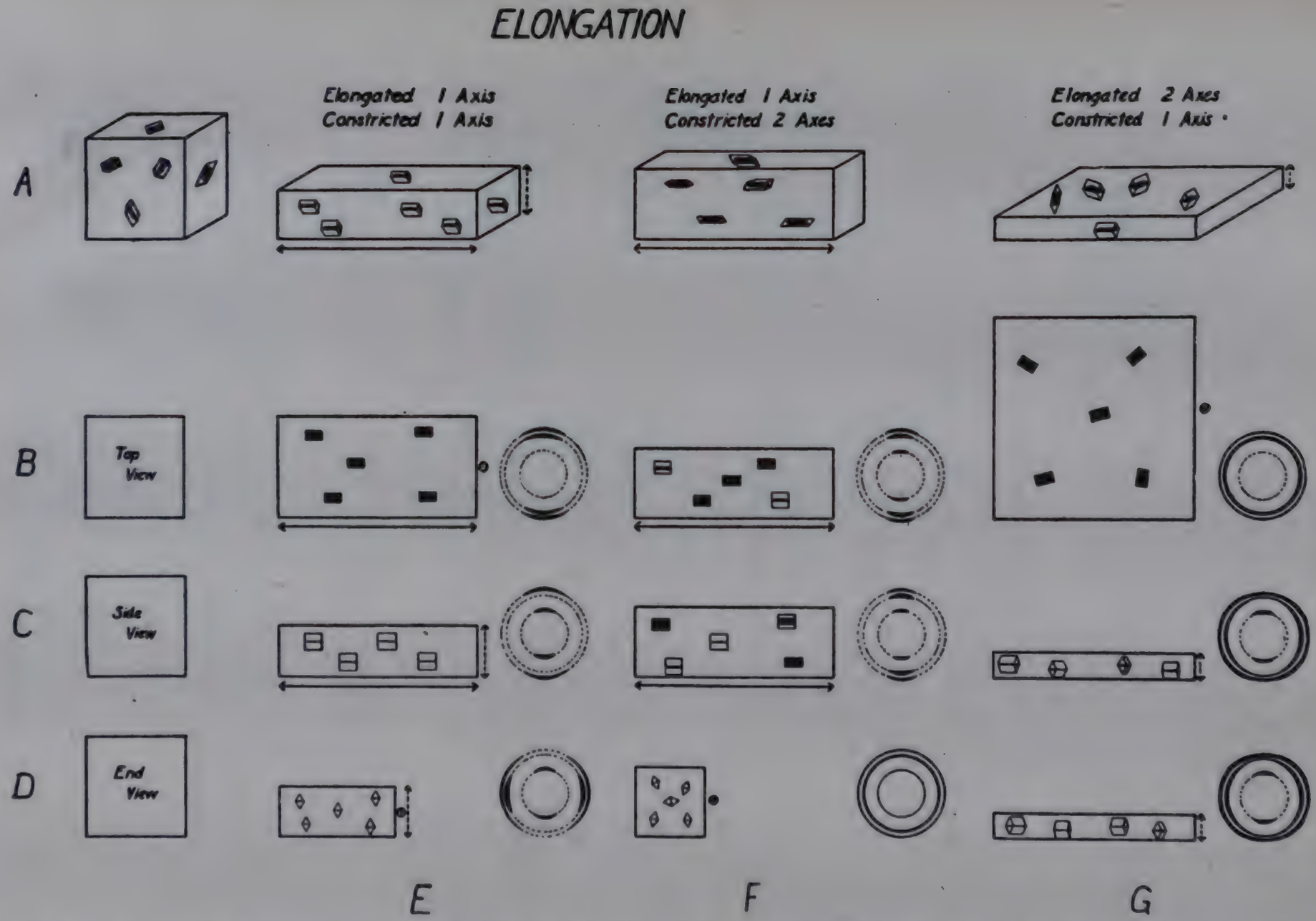

FIG. 21.—SCHEMATIC REPRESENTATION OF TYPES OF ORIENTATION AND CORRESPONDING X-RAY DIAGRAMS OBTAINED WHEN SWOLLEN HYDRATE CELLULOSE IS DEFORMED ALONG VARIOUS AXES (SISSON[107]).

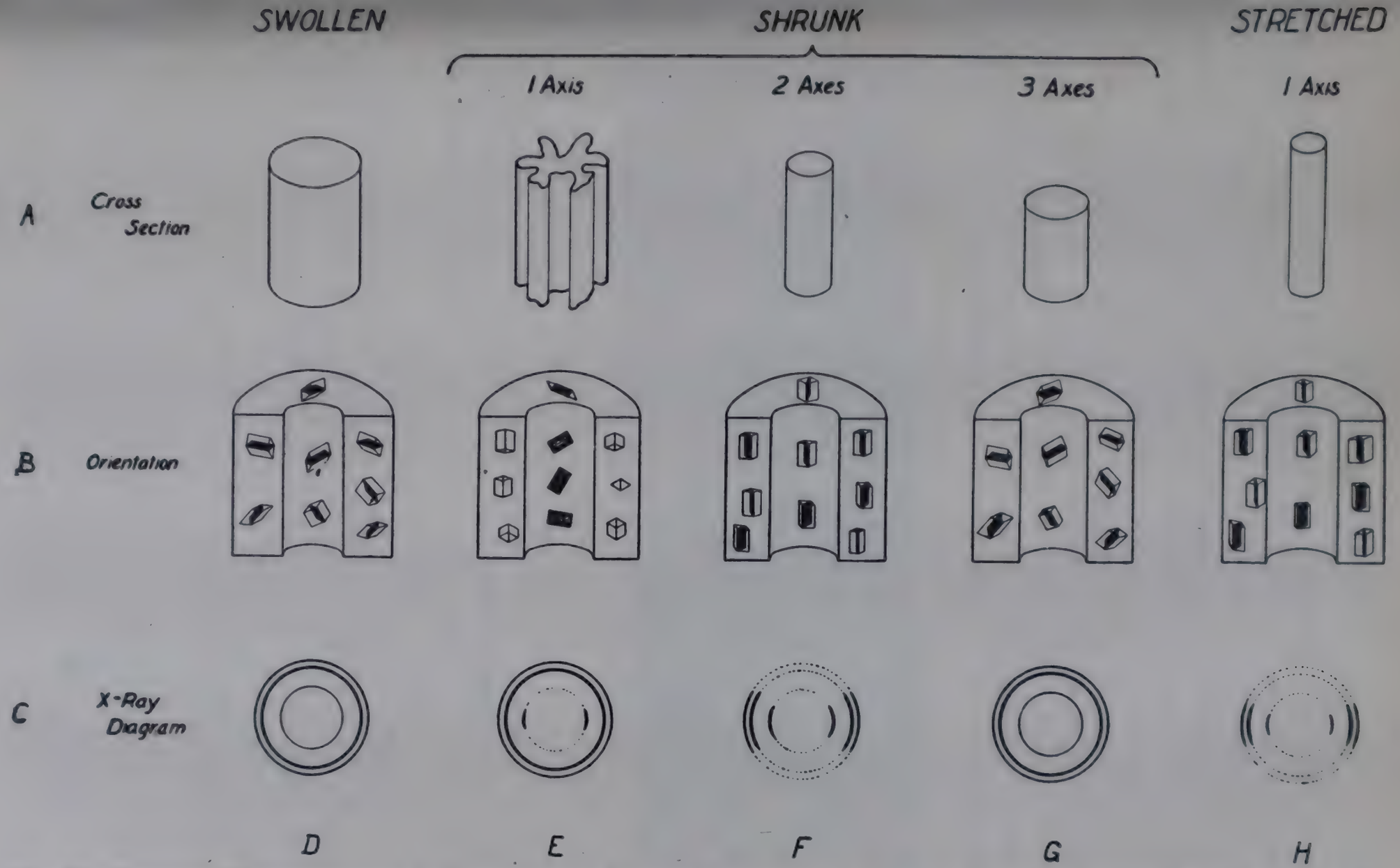

FIG. 22.—SCHEMATIC REPRESENTATION OF CROSS SECTION, TYPE OF ORIENTATION, AND X-RAY DIAGRAM OBTAINED WHEN RAYON FILAMENTS SHRINK ALONG VARIOUS AXES (SISSON[107]).

either reinforce or oppose each other, thus complicating the situation and making it difficult to evaluate the factors which influence the production of orientation. Many early workers have assumed that the orientation present in rayon filaments is produced before coagulation, while the viscose is passing through the spinneret, and that the role of the coagulating agent is primarily to "fix" the orientation already present. Although orientation may be produced in the spinneret, as evidenced by the stream double refraction of viscose in passing through an orifice, it is probable that this affects primarily the orientation of the chains to form a crystallite (crystallization). Experimental evidence[107] indicates that the degree and type of shrinkage are the more important factors in producing the final crystallite orientation in the dried filament. The composition and length of spinning bath, rate of spinning, and filament diameter all have a pronounced influence, but here, too, the orientation can be correlated to a certain degree with the change in dimensions of the fiber during the coagulating and drying process.

In Figure 22 there is represented diagrammatically the cross section (Fig. 22AD), orientation (Fig. 22BD), and the x-ray diagram (Fig. 22CD) of a swollen rayon fiber. Although shrinkage along one axis could occur in either the longitudinal, tangential, or radial direction, only the latter possibility will be considered. Since the circumference of the fiber does not change, the cross section could assume any shape between the serrated type (Fig. 22AE) and a flat ribbon-like type. As pointed out in a previous section, radial shrinkage should produce a selective uniplanar orientation with the (101) planes parallel to the filament surface and the *b* axes randomly arranged in a plane parallel to the surface. With the x-ray beam perpendicular to the fiber axis, the 101 line should exist as equatorial reflections and the $10\bar{1}$ as a random orientation (Fig. 22CE).

In the case of shrinkage along two axes, there are also three possibilities, only one of which is represented: shrinkage in the radial and tangential direction (Fig. 22AF). This produces a uniaxial orientation with the *b* axes parallel to the fiber axis; all three planes diffract as intensity maxima on the equator (Fig. 22CF).

Shrinkage along three axes (Fig. 22AG) can occur in only one way to produce a random orientation.

In the case of elongation, there is only one direction in which a rayon fiber can be stretched, in the direction of the fiber axis, which tends to produce a uniaxial orientation (Fig. 22AH). In practice, however, any combination of the seven shrinkage possibilities may have begun to occur or may be in the process of occurring while elongation is taking place, giving a

large number of possibilities, the detailed discussion of which space does not permit.

Each type of orientation illustrated in Figure 22 has been produced experimentally. Figure 23A is the x-ray diagram of a viscose fiber spun and allowed to dry without tension. All of the diffraction lines show a random orientation. Figure 23B is a fiber spun under the same conditions, with the exception that the ends of the fiber were fastened to a support immediately after coagulation so that longitudinal shrinkage was prohibited. The 101 diffraction line shows some orientation, while the $10\bar{1}$ and 002 have a random orientation. This type of orientation is characteristic of a selective uniplanar orientation (Fig. 22CE) which would result if shrinkage were

A B C

FIG. 23.—X-RAY DIAGRAMS OF VISCOSE FIBERS SPUN UNDER VARIOUS CONDITIONS (SISSON[107]).

(A) Allowed to shrink freely; (B) not allowed to shrink in length; (C) stretched and dried under tension.

confined largely to the radial direction, and it is typical of the x-ray diagrams given by the older types of viscose rayons. In Figure 23C the fiber was stretched and allowed to dry under tension. All of the x-ray lines exist as equatorial arcs indicating a uniaxial orientation, which is typical of the modern viscose fiber. If the rayon shown in Figure 23B is moistened and slowly stretched, the selective orientation is gradually changed to a uniaxial orientation. The effect of a hydrogen-bonding plasticizer, such as water, in assisting orientation is illustrated by the fact that stretching dry cellulose does not increase the preferred orientation.

A comparison of the x-ray orientation values with microscopic data, obtained either from refractive index measurements[108] or dichroism of fluo-

[108] R. D. Preston, *Trans. Faraday Soc.*, **29**, 65 (1933).

rescent dyes,[109] indicates that the optical methods measure the orientation of the skin, while the x-rays give a summation of the orientation throughout the filament. Optical and x-ray orientation values agree only on highly stretched fibers which have a high degree of parallel orientation throughout the fiber.

Relationship of Orientation to Physical Properties. The reported effect of increasing the orientation on some fiber properties are listed in Table 2

TABLE 2

EFFECT OF INCREASING ORIENTATION ON SOME FIBER PROPERTIES

Increases	Decreases	Little or no effect
Tensile strength	Total elongation	Sorption of water vapor
Transverse swelling	Reversible elongation	Elastic limit
Recovery after wet stretching	Longitudinal swelling	
Young's modulus	Dye absorption	
Rigidity	Plasticity	
Refractive index	Creasing resistance	
Gloss	Chemical reactivity	

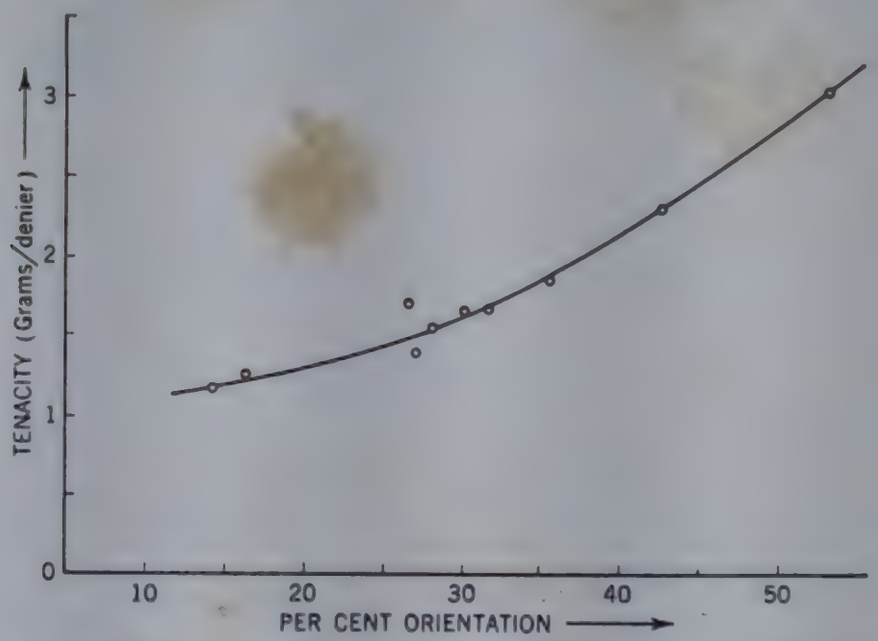

FIG. 24.—RELATIONSHIP OF TENSILE STRENGTH TO ORIENTATION.

The relationship of orientation to tensile strength and to extensibility for several samples of viscose rayon are shown in Figures 24 and 25, respectively.

[109] D. R. Morey, *Textile Research*, **4**, 491 (1934); **5**, 483 (1935).

In considering the effects of orientation on the properties of rayons, however, it is difficult to isolate crystallinity from orientation, since both occur simultaneously during spinning, each influencing the production of the other. Under a given set of conditions the effect of orientation on a given physical property can be demonstrated quite clearly, but a sweeping generalization cannot be made. It is possible to obtain two rayons which have the same degree of orientation but differ widely in their physical characteristics. As a general rule, a physical property such as tensile strength, which increases with orientation, may be correlated with the measured orientation provided the tensile strength values have a definite correlation

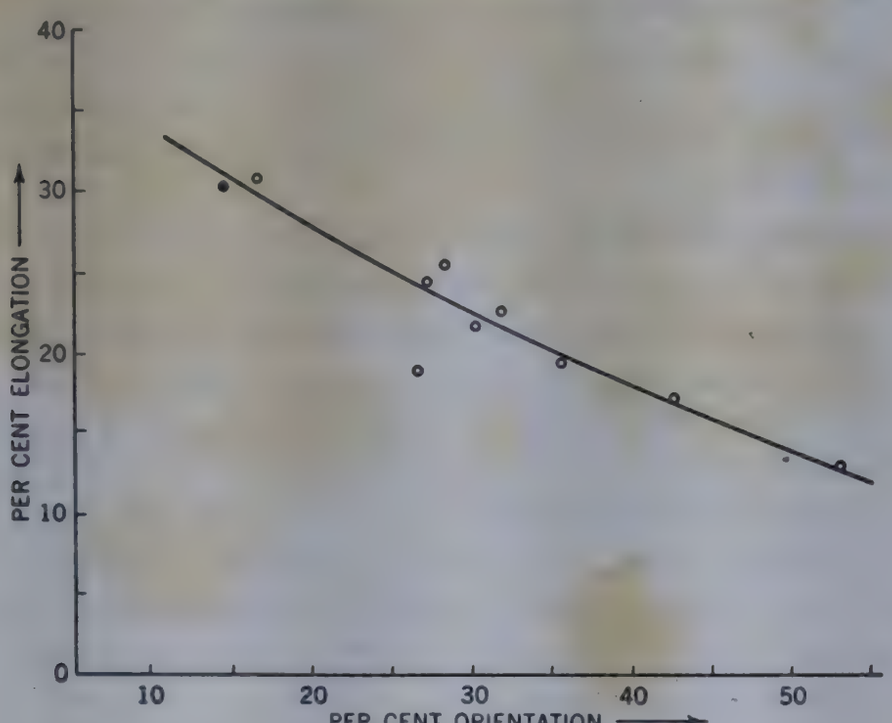

FIG. 25.—RELATIONSHIP OF TOTAL ELONGATION TO ORIENTATION.

with some other property, such as extensibility, which decreases with orientation. For example, if a rayon sample having a low tensile strength does not show a corresponding high extensibility, then the low tensile value is probably due to factors other than to a low degree of orientation.

The effect on tensile strength of factors other than orientation is illustrated by comparing viscose and cuprammonium rayons. The tensile strengths and extensibilities of each may be correlated with orientation, but the two rayons give separate curves, and, for a given degree of orientation, viscose fibers have higher strengths and greater extensibilities. According to Hermans,[61] the essential properties and quality of regenerated fibers depend on (1) the degree of polymerization and the distribution of chain

length, (2) the preferred orientation of the crystallites and molecules and the distribution of this orientation, (3) the ratio of crystalline to noncrystalline material, and (4) the average distribution of the above over the cross section of the fiber.

Cellulose Derivatives. It is possible to prepare many derivatives, including the nitrates and acetates, with the original fiber structure. The effect of substitution on the fiber diagram has been pointed out in the case of nitrocellulose from ramie which, up to 7.5% nitrogen, gives the fiber diagram of the original ramie; between 7.5 and 10.3% nitrogen the fiber is physically disintegrated, and an indefinite diffraction pattern is obtained. The parallel arrangement of the chains in this amorphous nitrate, however, is thought to exist, since the regenerated cellulose is in a fibrous form. Above 12.8% nitrogen a definite fiber pattern is obtained. Methylcellulose and cellulose acetate also give fiber diagrams as the trisubstituted product is approached.

Unstretched films of cellulose acetate and nitrocellulose show the occurrence of spontaneous orientation with reference to the surface, which is analogous to the previously discussed behavior of regenerated films. When films are swollen with an organic solvent and stretched or dried under tension, the x-ray diagram shows an orientation in the direction of tension. After the films are stretched in one direction, a second stretching at right angles destroys the first orientation, and a still further stretching in the new direction produces an orientation in that direction. In many cases, the type of orientation resulting from a given type of shrinkage or deformation is the same as that produced in swollen native or regenerated cellulose when subjected to similar treatment.

2. Cellulose Fiber Reactions

Many of the important chemical reactions of cellulose have a pronounced influence on the physical and chemical properties of the fiber, yet scarcely affect the x-ray diagram. For example, when cellulose is hydrolyzed with concentrated hydrochloric acid or oxidized with chromic acid, there is no change in the x-ray diagram even after the fiber has been reduced to a powder. This indicates that the reaction is intercrystalline in nature and does not change the internal structure of the crystallite. Other reagents may completely destroy the crystalline pattern, as, for example, when cellulose is oxidized with periodic acid. No new lines are produced, but the original crystalline pattern becomes more diffuse as oxidation proceeds.[110] This in-

[110] G. F. Davidson, *J. Textile Inst.*, **32**, T109 (1941).

dicates that the attack of periodic acid is not limited to the intercrystalline parts, as is the case for hydrochloric and chromic acids, but that the crystalline regions are gradually opened up and destroyed as oxidation proceeds.

The type of cellulose reactions to which x-ray diffraction analysis may be applied most profitably are those involving a change in crystal structure rather than those involving no effect or complete destruction. X-ray studies of a reaction involving a change in structure give information regarding the mechanism of the reaction as well as the structure of the reaction product. Examples which will be discussed in the present section are cellulose derivatives, swelling, crystalline addition compounds, mercerization, and hydration. In discussing these reactions, no attempt will be made to consider all the chemical evidence. To do so would be a repetition of material presented elsewhere in this book. The discussion, therefore, will be limited to certain x-ray data, which, in the author's opinion, help to elucidate the role of fiber structure in many complicated cellulose reactions.

(*a*) *Cellulose Derivative Formation*

It is difficult to classify satisfactorily the changes that take place in the x-ray diagram paralleling derivative formation, but it is often possible, as in the typical case of acetylation, to distinguish three more or less overlapping phases[111]: (1) only the cellulose diagram is present, (2) the interferences of the product of the reaction appear superimposed on the cellulose diagram; and (3) finally the cellulose interferences disappear and only those of the product of the reaction remain. In some cases the second phase of the reaction does not consist of two superimposed diagrams but of a disorganized or amorphous x-ray diagram. For example, the diagrams of nitrated ramie between 7.5 and 10.3% nitrogen are indefinite or amorphous.

Reaction Mechanism. During the early history of x-ray diffraction analysis of cellulose derivatives, the data were thought to indicate all of the lower derivatives to be mixtures of cellulose and its trisubstitution product. At present the most widely accepted explanation of the changes in the x-ray diagram is on the basis of a heterogeneous micellar reaction. If the fiber is reasonably well purified, it is assumed that the reagent penetrates the fiber, attacking first the surface of the crystallite which is changed into the trisubstituted derivative; it then proceeds inward, producing between the unreacted interior and the completely reacted surface a partially reacted area in which only one or two hydroxyl groups for each

[111] W. A. Sisson, *Ind. Eng. Chem.*, **30**, 530 (1938).

glucose unit have been replaced. This partially reacted area may produce an amorphous diagram, whereas the product of the reaction would yield only its characteristic x-ray diffraction diagram when several molecular layers have been formed. It is further assumed that some crystallites have reacted to a greater degree than others, as supported by the fact that x-ray diagrams of certain acetates formed from native cellulose show the interference of both native and cellulose hydrate upon hydrolysis. Furthermore, in some cases it is possible to fractionate with organic solvents and obtain fractions showing different x-ray diagrams. In many cases, however, it is impossible to fractionate the reaction mixture, and this has been explained on the assumption that some of the glucose residues of a single chain are completely acetylated, some are partly acetylated, and some have no acetyl groups at all.

The mechanism of derivative formation, however, cannot in all cases be explained on the basis of a micellar heterogeneous reaction. The heterogeneous nature of the reaction is due in many cases to both fiber and micellar structure, especially if the reaction is not allowed to proceed to equilibrium. Examination of incompletely nitrated cellulose fibers by means of the polarizing microscope has been claimed[112, 113] to show the coloration of the fiber surfaces to be that of a trinitrate, whereas the interior is characteristic of a lower nitrate, indicating heterogeneity. Similar results on benzylation have been obtained with ordinary light.[114] The heterogeneity, therefore, may mean that there is a random arrangement of the substituted groups along the chains of glucose residues and that the external chains of the crystallite and the outer sections of the fiber are more highly substituted than the interior.

Other reaction mechanisms have been offered, but it would appear that all x-ray data might be adequately explained by quoting from a recent paper.[114] "There is evidence to support the view that cellulose reactions do not follow a single pattern, and that the type varies, depending on the reaction partner, its concentration, the reaction medium, temperature, etc. It is quite probable that all the reaction models, worked out for micro-heterogeneous systems, such as surface reactions, topochemical macro-heterogeneous reactions, permutoid or quasi-homogeneous reactions, as well as the previously mentioned micellar heterogeneous reactions, may apply to cellulose in one case or another, depending on circumstance."

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[112] J. Desmaroux and M. Mathieu, *Compt. rend.*, **192**, 234 (1931).

[113] K. Hess, *Die Chemie der Zellulose und ihrer Begleiter*. Akademische Verlagsgesellschaft m. b. H., Leipzig, 1928, p. 360.

[114] E. J. Lorand and E. A. Georgi, *J. Am. Chem. Soc.*, **59**, 1166 (1937).

The nature of the heterogeneous reactions is closely associated with the rate of formation which in general depends on the velocity of diffusion, speed of surface reaction, and nature of the surface layer formed by the reaction product. X-ray analysis indicates that the kinetics of the cellulose derivative formation are determined largely by the velocity of diffusion rather than by the speed of the chemical reactions. Thus, at the first stage the rate is determined by the nature of the intermicellar spaces through which the reagent becomes accessible to the micellar surfaces. In the second and last phase the reaction progresses from the surface of the micelle to the interior, and at this stage the rate depends largely on the permeability of the reacted layer to the reactant molecules. The reaction rate may be increased by several so-called processes of cellulose activation. For example, at the first stage, swelling of the fiber may promote the rate of diffusion by enlarging the intermicellar spaces and rendering the surface of the micelles more accessible. At the second stage, the rate may be increased by the formation of alkali celluloses or any other compound which enlarges the lattice spacings and thus permits faster diffusion into the crystallite. At the last stage the rate may be increased by substances which form a double compound with the reaction product and thus enlarge the lattice spacings of the reacted layer.

Structure. Owing to the lack of single crystals and often fiber patterns, very little definite information is available regarding the unit cell structure of cellulose derivatives. In general the original arrangement of the cellulose chains is not greatly disturbed by the formation of substitution products. The chains remain parallel to one another and at well-defined distances which depend on the size of the substituted group and the completeness of substitution. For example, in passing from the triacetate to the tristearate, the spacings along the cellulose chains do not change, but the distances between the chains increase as the number of carbon atoms in the aliphatic chains increases.

The exact arrangement of the substituted groups is largely a matter of assumption. The aliphatic chains of cellulose polyesters are almost perpendicular to the direction of the principal valence or cellulose chains just as in the pentaacetic, pentalauric, and pentapalmitic esters of glucose. These latter esters form fibers in which the aliphatic chains are arranged at right angles to the length of the fiber. In a homologous series the side bonds of the cellulose lattice are progressively weakened by replacement of hydroxyl groups with aliphatic chains and the crystalline character becomes less and less apparent. In native cellulose the fiber period of 10.3 Å. corresponds to two glucose units. In most cellulose derivatives it has the same

value; but when it differs, the period is a multiple of 5.15 Å. which is the length of one glucose unit, the factors being 2, 3, 4, and 5. The 5.15 Å. value seems to have a closer relation to the constitution of cellulose derivatives than the 10.3 Å. value.

Many cellulose derivatives do not always have the same unit cell structure but exhibit the property of polymorphism. For example, methylcellulose can be changed into a different form by heating. Likewise, when trinitrocellulose is dissolved in acetone and evaporated, a new crystal structure is formed as a result of passing through the dispersed phase. One of the most widely discussed examples of polymorphism is cellulose acetates I and II which are transformed into each other reversibly, the equilibrium depending upon the temperature and the solvent.

(*b*) *Swelling*

Swelling is a characteristic which usually proceeds, and is closely associated with, most cellulose reactions. Since cellulose is hydroplastic rather than thermoplastic, swelling is also closely associated with most stretching and forming operations which are necessary for the production of strong regenerated films and fibers.

According to Katz,[115] a solid is said to swell when it takes up a liquid, while at the same time (1) it does not lose its apparent (microscopic) homogeneity, (2) its dimensions are enlarged, and (3) its cohesion is diminished; that is, it becomes soft and flexible.

Swelling is to be distinguished from capillary imbibition, such as is shown by a solid having many fine capillary canals. A porous tile, for example, will take up liquids, but it is nonhomogeneous, its dimensions do not change, and its cohesion is not diminished. When the order of magnitude of the capillary tubes, however, becomes very small, there may exist phenomena lying halfway between the two extremes of swelling and capillary imbibition. This, in addition to real swelling, is exhibited by cellulose.

Solids which are capable of swelling consist, in a great many cases, of substances of high molecular weight. Furthermore, many, including cellulose, are built up of a large number of minute, discontinuous crystalline areas (crystallites) which are separated by areas of less crystallinity. These high-molecular-weight substances having a micellar structure are to be contrasted to low-molecular-weight substances which exist as definite crystals, where there is often no distinct swelling stage between the solid and solvated condition. Materials exhibiting swelling behavior frequently

[115] J. R. Katz, *Trans. Faraday Soc.*, **29**, 279 (1933).

have their degree of swelling limited by the presence of polar groups which bond the high-molecular-weight chains together. As a corollary, it follows that any liquids which cause swelling of cellulose must be capable of breaking these secondary valence bonds between the high-polymer molecules and of forming their own bonds with the polymer. It also follows that in any substance which contains both crystalline and amorphous areas, it will be more difficult for the swelling liquid to disrupt the dense bond network of the crystalline areas than to disrupt the more scattered and weaker bonding of the amorphous areas.

Since cellulose fibers are porous solids of high molecular weight, the molecules of which are held together by at least four types of bonds (van der Waals', polar, hydrogen bonds, and primary valence bonds) to form minute crystalline and amorphous areas, which often harbor numerous noncellulosic constituents, it is obvious that cellulose fibers fulfill all of the conditions for complex swelling, capillary imbibition, and other intermediate phenomena.

Types of Swelling. Since cellulose contains both crystalline and amorphous areas, it is of importance to know whether the liquid penetrates the interior of the crystallite or only the intercrystalline areas. When the liquid penetrates only the intercrystalline areas, there should be no change in the crystalline pattern, and all that happens is that the amorphous diagram of the liquid appears superimposed upon the crystalline diagram. When the crystalline x-ray diagram is different before and after swelling, it is quite definite that the liquid has penetrated the interior of the crystallite. Katz[115] has classified these two types of swelling as "inter-" and "intra-micellar" swelling, respectively. In the present discussion these terms will be used interchangeably with the terms "inter-" and "intra-crystalline" swelling.

In fibers where the crystalline and amorphous areas gradually merge, as in regenerated fibers, it is difficult to draw a sharp distinction between the two areas, and one is not entitled, therefore, to draw from the unchanged crystalline x-ray diagram the conclusion that the liquid did not partially penetrate into the interior of the micelle; if only a few layers of molecules are penetrated, the change in ratio of crystalline to amorphous pattern cannot be detected.

In the case where the crystalline x-ray diagram is changed (intramicellar swelling) it is possible to distinguish two cases: (1) The dimensions of the unit cell of the crystallites are enlarged according to a continuous function of the degree of swelling. If the change in dimensions of the fiber can be explained on the basis of the change in unit cell dimensions then one can

say that the swelling is chiefly intramicellar. (2) There is a marked change in the x-ray diagram, but this change is not a continuous function of the degree of swelling. The original crystalline diagram loses intensity as a definite new one is formed. In this case it must be assumed that the liquid forms a compound with the crystalline cellulose and that the original unit cell structure is changed into a new unit cell structure characteristic of the compound. The nature of this compound formation will be discussed later. As a general rule, the unit cell enlargement is small compared to the fiber swelling, in which case the fiber swelling is not entirely explained by the change in x-ray diagram. The additional fiber swelling is due to intercrystalline swelling, and the change in crystal structure is only an accessory phenomenon in the mechanism of fiber swelling. Katz[115] has referred to this type of swelling as "permutoid" swelling. Most of the swelling of cellulose fibers by strong alkalies (*e. g.*, mercerization) are of the "permutoid" type.

Inter- and intra-crystalline swelling may be divided further into two subdivisions: limited and unlimited swelling. Limited swelling may be said to occur when there is a maximum to the amount of liquid taken up (*e. g.*, as with 18% NaOH), while with unlimited swelling the swelling gradually changes into solution (*e. g.*, as with cuprammonium hydroxide).

Dispersion may thus be considered as the condition of extreme or unlimited swelling: the separation of the crystallites or molecules to such an extent that there is little or no attraction or cohesion between them. On the basis of the two types of swelling, intra- and inter-, it is theoretically possible, therefore, to have either a molecular or micellar dispersion. In the case of molecular dispersion, unlimited swelling for both inter- and intramicellar swelling must occur; for micellar dispersion, there must be unlimited intermicellar swelling but limited intramicellar swelling. Dispersions due to intermicellar swelling alone seldom occur since cellulose regenerated from its dispersions usually has the hydrate crystalline structure, concerning which more will be said later. Exceptions are strong hydrolyzing or oxidizing intermicellar swelling agents which may produce dispersion as a result of degradation to a more soluble product.

Relationship of Swelling to Microscopic Structure. Inter- and intramicellar swelling, as indicated by the x-ray diagram, can be correlated with the fiber and the fibril swelling of native fibers. Comparative x-ray and microscopic studies on fibrils isolated from young cotton fibers[73] indicate that in the case of intermicellar swelling, such as produced by water or weak acids and alkalies, the diameter of the fibril is not appreciably changed. Most of the fiber swelling apparently takes place in the amor-

phous phase between the fibrils. This swelling or taking up of liquid by the interfibril phase would account for the appearance in the x-ray diagram of an amorphous pattern which is superimposed upon the original crystalline cellulose pattern.

With intramicellar swelling of the limited type, such as produced by ethylenediamine[116] where there is the appearance of a new crystalline pattern corresponding to the formation of a swelling compound, the fibril may be observed to increase in diameter. This increase in fibril diameter is of the same order of magnitude as the lateral increase in the unit cell dimensions calculated from the x-ray diagram[73] which would indicate that most of the fiber swelling may be accounted for by the intramicellar swelling or compound formation. The formation of a swelling compound does not destroy the double refraction of the fibril and, after swelling has once taken place, there is no further swelling of the fibril or change in the x-ray diagram with further application of the swelling agent. Intramicellar swelling is also produced by strong alkalies, but here it is accompanied by excessive fiber swelling and the appearance of a pronounced liquid pattern superimposed upon the crystalline pattern of the new swelling compound. In this case the liquid pattern and most of the fiber swelling may be accounted for by simultaneous swelling of the interfibril material.[117]

In the unlimited type of intramicellar swelling, such as produced by strong sulfuric acid, where the crystalline pattern disappears completely, microscopic examination shows the fibril to swell in diameter with the disappearance of double refraction. In this type the swelling is progressive with further addition of reagent until the fibril is disrupted. It must be remembered, however, that hydrolysis always occurs simultaneously with sulfuric acid swelling.

From the preliminary x-ray and microscopic results now available it would appear that the terms "inter- and intra-fibril" swelling may be used synonymously with the terms "inter- and intra-micellar" or "inter- and intra-crystalline" swelling. The anisodimensional swelling of cellulose fibers can be explained in almost every case on the basis of variation in orientation of the fibril units.

Owing to the absence of a visible structure for regenerated cellulose, no microscopic correlations can be made with the x-ray data. In general, however, the hydrate crystal lattice of regenerated cellulose is much more readily penetrated than is the native lattice, and as a result many reagents which may be considered as intermicellar swelling agents for native cellulose

[116] C. Trogus and K. Hess, *Z. physik. Chem.*, **B14**, 387 (1931).

[117] W. A. Sisson and W. R. Saner, *J. Phys. Chem.*, **43**, 687 (1939).

become intramicellar when applied to hydrate cellulose. Furthermore, the greater percentage of amorphous cellulose in regenerated fibers makes them more susceptible to the penetration of most liquids, and it is probable that swelling in the amorphous areas would serve as a wedge to gradually open up and produce partial swelling of the crystalline areas. If the crystalline x-ray diagram of a regenerated fiber remains unchanged during swelling, it can only be concluded that the interior of the crystalline areas does not change in structure, and it is impossible to say how far the swelling agent has penetrated the outer boundary areas of the crystallite.

The capillary structure of native and regenerated cellulose is also different. In native fibers the capillary structure is largely a function of the morphological structure and the fibril orientation. Random orientation means looser packing of the fibrils and hence a more porous structure. Regenerated fibers have a very fine capillary structure which is a function of the orientation and of the ratio and relationship of crystalline to amorphous material.

Swelling Theories. Several theories have been advanced which are concerned with the taking up of a swelling medium by a swelling solid. The following mechanisms, which have been discussed in greater detail by Stamm,[118] may be considered as typical, although none of them are entirely satisfactory.

(1) The absorbed ions, together with the immobilized ions of opposite charge which remain in close proximity to the absorbed ions, bring their sphere of water with them. This water hydration of the ions is thought to be responsible for the swelling of the solid. This theory is applicable for aqueous swelling agents.

(2) The electrical charge set up on the surface, due to selective absorption of ions or molecules, results in a repulsion of the like surface charges which allows water to enter mechanically. This theory is applicable for water, dilute aqueous solutions, and nondissociated organic liquids, but not to concentrated aqueous solution of electrolytes.

(3) A Donnan membrane equilibrium is set up which results in a higher concentration within the membrane than on the outside and a subsequent taking up of water by osmosis due to concentration differences. This theory assumes the presence of diffusable electrolytes in solution and an appreciable ionization constant of the swelling material. None of the theories are generally applicable to explain all of the experimental data regarding all forms of cellulose swelling.

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[118] A. J. Stamm, U. S. Dept. Agr., *Misc. Pub.* **240** (1936).

Examples of Intermicellar Swelling. When cellulose swells in water the volume of the solid is increased, but the total volume is less than that of the original solid plus the liquid. Since x-ray patterns show no change in the crystal lattice, the volume change must be associated with the intermicellar swelling. The change is believed to be due to a compression of the water and cellulose molecules caused by the attraction of the water molecules by the hydroxyl groups of the cellulose. Since the crystalline pattern of cellulose is not affected by water, it has been commonly assumed that water does not penetrate the crystalline areas. Exchange reactions of cellulose and heavy water,[119] however, indicate that heavy water, and hence ordinary water, must penetrate throughout the mass of cellulose, including the crystallites.

Organic liquids, in general, swell cellulosic materials less than water, the swelling being proportional to the polarity of the liquid. Normal alcohols give a decreased swelling with an increase in molecular weight while nonpolar hydrocarbons produce no swelling at all. Swelling in benzene is negligible[120] but a series of benzene derivatives give increasing swelling in the order $H<CH_3<NH_2<CHO<Br<Cl<NO_2$, which is the same order as that of the increasing dipole moments of the liquids.

Water-swollen regenerated cellulose may be made to retain a considerable proportion of its swollen dimensions upon drying if the water is replaced by a water-miscible liquid, such as alcohol, which in turn is replaced by ether or acetone and the latter by a nonpolar liquid such as benzene or propane.[121] If these aerogels are wet with water they shrink greatly during subsequent drying.

Swelling beyond the normal water-swollen dimensions takes place when cellulosic materials are treated with certain aqueous acid, basic, or salt solutions. The order of swelling power of the salts follows the well-known lyotropic series, the more hydrated ions being the most effective swelling agents. The decreasing order of swelling is as follows[118]:

$$Zn>Li>Ca>Mg>Mn>Ba>Na>NH_4>K$$

$$CNS>I>CrO_4>Br>Cl>NO_3>SO_4>ClO_3$$

As a rule cellulose swells more in alkalies than in acids, but the *p*H of a salt solution appears to have little effect upon its ability to cause swelling.

In addition to acids, bases, and salts which are strong electrolytes, swell-

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[119] G. Champetier and R. Viallard, *Bull. soc. chim.*, [5], **5**, 1042 (1938).

[120] A. J. Stamm, *Ind. Eng. Chem.*, **27**, 401 (1935).

[121] S. S. Kistler, *J. Phys. Chem.*, **36**, 52 (1932).

ing beyond the water-swollen condition is also produced by a considerable number of nondissociated organic substances, such as thiourea, chloral hydrate, resorcinol, and benzene sulfonates.[115] Many organic compounds containing sulfur ($S^{=}$) or a halogen are effective swelling agents in aqueous solution. Katz[115] has suggested that the sulfur and halogen groups are bound up by the free cellulose hydroxyl groups, while the other polar groups of the molecule in turn bind water, thus accounting for the increased swelling. The atomic groupings $R\begin{matrix}N< \\ N<\end{matrix}$ or >N—N< have a strong affinity for cellulose and hence produce swelling.

Examples of Intramicellar Swelling. Most strong bases and acids and a few salts produce both inter- and intra-crystalline swelling, the latter occurring only at high concentrations. The action is usually specific as to whether the swelling is limited or unlimited. When the intracrystalline swelling is of the limited type a definite swelling compound is formed, the nature of which will be discussed in a later section.

Alkali reagents such as strong (18%) sodium hydroxide produce both inter- and intra-crystalline swelling of the limited type, as indicated by the appearance of a new x-ray diagram (soda cellulose), and an increase in fiber diameter greater than that explained by the expansion of the crystalline lattice resulting from the formation of the soda cellulose. Ethylenediamine produces a marked intracrystalline swelling of the limited type, as evidenced by the appearance of a new x-ray diagram[116] and, since the lattice expansion is of the same order as that of the fiber as a whole, the swelling is said to be largely of the limited intracrystalline type. Liquid ammonia likewise reacts with cellulose to produce intramicellar swelling,[122] but it differs from the amines in that the lattice expansion is a function of the ammonia content.[123]

Strong acids, such as sulfuric (72%) and phosphoric (83%), produce an unlimited intracrystalline swelling[73] and the lattice is expanded in a heterogeneous manner, as evidenced by the absence of definite diffraction lines. The original equatorial lines of a well-oriented fiber spread gradually in the form of a streak across the equator as swelling progresses. In addition to chemical hydrolysis produced by acids, a further difference in alkali and acid swelling may be noted in the microscopic results. With alkali swelling, the fibril swells but still retains its birefringence, while swelling with acid, the fibril swells greatly in diameter and gradually loses its birefringence. The mechanism of swelling in nitric acid apparently shows

[122] A. J. Barry, F. C. Peterson, and A. J. King, *J. Am. Chem. Soc.*, **58**, 333 (1936).

[123] G L. Clark and E. A. Parker, *J. Phys. Chem.*, **41**, 777 (1937).

greater similarity to alkali swelling since it is said to form a definite swelling (Knecht) compound.[124]

The alkali swelling agents, such as the quaternary ammonium hydroxides and cuprammonium hydroxide, which are dispersing agents for cellulose, produce both inter- and intra-crystalline swelling. As to whether both types are limited or unlimited depends upon the nature of the reagent. With the quaternary ammonium hydroxides, the fiber-swelling reaction, which proceeds rather rapidly, is characterized by a relatively high rate of diffusion of the base throughout the fiber and an apparent equal modification of all the crystalline cellulose that reacts with the base to form a swelling compound. X-ray patterns show the swelling compound to be formed before appreciable increase in fiber diameter takes place, and after the swelling compound is formed, further addition of the swelling reagent produces no additional lattice expansion, while the fiber diameter continues to increase. This continued increase in fiber diameter is apparently due to swelling of the intercrystalline material. The over-all swelling reaction, therefore, may be thought of as a dual process; the crystalline cellulose apparently has a limited increase in volume, while the intercrystalline material has no limit. All of the quaternary ammonium hydroxides produce definite swelling compounds (limited intramicellar swelling), but appreciable unlimited intermicellar swelling is obtained only when large substituents are present as in dibenzyldimethylammonium hydroxide. Likewise, the greater swelling and dispersion of degraded cellulose in sodium hydroxide may be considered as a greater unlimited intermicellar swelling made possible by the larger number of main valence chains which end in the intercrystalline areas of degraded native cellulose.

Frequently, in the case of alkaline solvents incomplete solution is observed. In this case, some of the fiber appears to disperse completely while some of the fiber structure is maintained. Usually, a clear-cut separation of dissolved from undissolved material is possible by settling or centrifuging. Of course, if the amount of solvent used is not greater than the volume to which the undispersed material can swell, it will be impossible to effect a separation of the dispersed from the nondispersed portions. Proper dilution will make possible the separation. If such a separation is carried out, the dispersed fraction appears to be molecularly dissolved while the undispersed fraction is highly swollen. This swollen state may be attributed to the same factors causing swelling in general; namely, partial solution of portions of molecules and a general loosening of the forces binding fibrils to one another.

[124] K. R. Andress, *Z. physik. Chem.*, **A136**, 279 (1928).

The dispersion of cellulose in cuprammonium hydroxide is preceded by unlimited intermicellar swelling. It has been reported that two cellulose-copper compounds are formed,[125, 126] which would indicate that the initial stages of cellulose dispersion in cuprammonium hydroxide should be micellar in nature, while the extent of the final dispersion, which is considered by most workers to be molecular, would probably depend on such factors as agitation, cellulose concentration, and the ammonia, nitrous acid, and copper content of the cuprammonium hydroxide.

Effect of Temperature and Concentration. With alkali hydroxides, as a general rule, greater swelling is produced at lower temperatures, the effect being greater the lower the concentration. With sodium hydroxide, for example, intracrystalline swelling is produced with a 6% solution at 0°C.; a 14% solution is necessary at room temperature, while at higher temperatures (70–80°C.) only partial swelling is obtained even with a 20 or 30% solution. Treatment at a higher temperature followed by a treatment at a lower temperature increases the swelling, but the swelling remains less than that of fibers treated directly at the lower temperature. On the other hand, treatment at a lower temperature followed by a higher temperature decreases the swelling very little. With quaternary ammonium hydroxides temperature has less effect, and the same is true of swelling with strong acids.

For most swelling agents there is a limited concentration below which there is little swelling. As the concentration is increased intercrystalline swelling first takes place, followed by intracrystalline swelling. For sodium hydroxide the minimum concentration at which intracrystalline swelling begins corresponds to the concentration for maximum intercrystalline swelling. For the other alkali hydroxides, the more basic the metal, the lower the minimum swelling concentration. With the quaternary ammonium hydroxides the minimum swelling concentration decreases with increasing molecular weight when the concentration is plotted in terms of normality. With most of the alkali swelling agents there is a range of several per cent (3–6%) concentration over which there is only partial intracrystalline swelling. With sulfuric acid, this range is very narrow (1%).

Orientation Effects. When a cellulose fiber is swollen, the tendency is to produce a more random orientation. In a well-oriented fiber, therefore, swelling would tend to increase the fiber diameter and decrease the fiber length, while a randomly oriented fiber would tend to swell uniformly in

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[125] K. Hess, C. Trogus, N. Ljubitsch, and L. Akim, *Kolloid-Z.*, **51**, 89 (1930).

[126] C. Trogus and K. Hess, *Z. physik. Chem.*, **B6**, 1 (1929).

all directions. For example, when a native fiber such as cotton, which possesses a spiral fibril structure, is swollen with sodium hydroxide, most of the change in fiber dimensions results from the fibrils being pushed apart laterally by the intercrystalline or interfibril swelling. In raw cotton another factor must be considered in that the over-all fiber swelling is restricted by the confining action of the cuticle. In a regenerated fiber where the intercrystalline swelling takes place both at the sides and ends of the crystallite, it is obvious that a liquid such as water, which produces only intercrystalline swelling, would increase both the fiber length and diameter. Thus in a rayon fiber, the over-all swelling for a given reagent is not only a function of the orientation but also of the dimensions of the crystallites and the ratio of crystalline to amorphous material.

Cellulose Derivatives. As a general rule, solvents for cellulose derivatives act first as a swelling, afterwards as a dispersing, agent. As with native fibers, swelling may be divided into that occurring as intermicellar, that occurring as intramicellar, and that osmotically conditioned.[111]

Intermicellar swelling depends on capillary action and does not affect the x-ray diagram; there is the simple condition of the halo interferences of the liquid being superimposed upon the diagram of the derivative.

Intramicellar swelling is characteristic of most cellulose esters and ethers with their solvents, but is often preceded by intermicellar swelling. For example, the diagrams of both the fibrous cellulose triacetate and the acetone-soluble modification show an increase in the amorphous scattering and a displacement of the equatorial interferences toward the center when treated with either acetone vapor or liquid. Likewise cyclohexanone, methanol, benzene, pyridine, or chloroform-methanol mixtures swell fibrous cellulose triacetate and produce an expansion of the lattice at right angles to the fiber axis.

Under osmotically conditioned swelling may be classified such processes as those in which the swelling compounds dissolve in the interior of the micelle, which is surrounded by an outer semipermeable sheath. Osmotically conditioned swelling is often preceded by other types. For example, triacetate when treated with chloroform first undergoes intramicellar swelling. Later, however, the spectrograms of the swollen fibers do not show interference lines but only the characteristic rings of the liquid used.

The examination of the swelling effect of organic liquids in many cases may be complicated by the presence of other factors. For example, when cellulose acetate is swollen in organic liquids, a different x-ray diagram is obtained at different temperatures. Likewise, the swelling of nitrocellulose

from ramie in organic solvents depends upon the concentration and nature of the solute as well as the previous treatment of the sample.

When the liquid is evaporated from fibers of trinitrocellulose or cellulose triacetate which have been changed by swelling in certain liquids, the altered x-ray diagram reverts reversibly to that of the original fiber. Likewise, the original pattern of nitrocellulose is regenerated when camphor, which causes the crystalline pattern of nitrocellulose to change to an amorphous pattern, is removed. If cellulose triacetate is treated with excess chloroform, beyond that necessary to produce swelling and distention of the lattice, the x-ray pattern gradually fades with dispersion in the solvent. It is thought that the intramicellar swelling is followed by disruption of the lattice to form solvated molecular fragments.

(*c*) *Swelling Compounds*

Intracrystalline swelling of the limited type, in most cases, results in a definite stereometrical relationship between the glucose units and the molecules of the swelling agent. This is referred to as a swelling compound or crystalline addition compound. These compounds are well known in cellulose chemistry, examples of which are "alkali cellulose" or "soda cellulose," the swelling compound formed between sodium hydroxide and cellulose, and the "Knecht compound" formed between cellulose and nitric acid. Swelling compounds are not necessarily the result of a chemical combination between the glucose unit and the swelling agent but may also result from secondary valence forces between the hydroxyl groups of the glucose unit and the swelling molecule. The molecules of the swelling agent, in either case, are distributed in a definite geometrical pattern throughout the expanded crystal cellulose lattice, and, as a result, swelling compounds always give a definite crystalline pattern which is characteristic for each swelling agent. In the present discussion, therefore, a swelling compound will be defined as a product which gives a definite crystalline x-ray diagram as a result of swelling, irrespective of the nature of the chemical reaction between the cellulose and the swelling agent. Swelling compounds, as a rule, are easily decomposed by water, the cellulose crystal structure reverting to that of hydrate cellulose.

Reagents Which Produce Swelling Compounds. Perhaps the best known example of swelling compound formation is the formation of soda cellulose. Carbon disulfide has been reported to react with soda cellulose I during xanthation to form a product that shows a characteristic x-ray

diagram,[127, 128] but this has not been confirmed by other workers,[129, 130] and there are indications that the intracrystalline swelling produced by xanthation may be of the unlimited type. Centola[129] concludes that the initial stages of the reaction involve only the surface of the crystallite, the distribution of the xanthate groups being frequently uneven, while continued formation of xanthate groups gradually brings about disintegration of crystalline structure. This is confirmed by other work[73] which indicates that as xanthation proceeds the diagram of the swelling compound, soda cellulose, is gradually replaced by a less definite, amorphous-like pattern.

When aqueous solutions of hydrazine, ethylenediamine, and tetramethylenediamine act on cellulose, swelling compounds are formed which give definite x-ray diagrams, the nature of which depends on whether native cellulose or mercerized cellulose is used as the starting material.[116] Nonaqueous alkyl amines have also been reported to react with cellulose to form swelling compounds.[131]

Ammonium hydroxide does not affect the lattice structure of cellulose, but it has been shown by several investigators[122, 123, 132, 133] that liquid ammonia reacts to form an ammonia cellulose complex, which has two modifications at $-20°$C. and $-30°$C. The ammonia cellulose complex formed at room temperature differs from the usual swelling compound in that the lattice extension is a function of the ammonia content.[123] When the ammonia cellulose is heated for several hours at 105°C., it loses its ammonia and gives a diffraction pattern which is very similar to that of mercerized cellulose. If the ammonia cellulose is decomposed by dilute acid or water, however, then the pattern of the regenerated cellulose is the same as that of the untreated material.

The quaternary ammonium hydroxides, with the exception of choline, form swelling compounds as indicated by the appearance of a new crystalline x-ray diagram.[117] Heat does not affect the spacings of the methyl- or ethyl-ammonium hydroxides but the 101 spacing is reduced for the benzyl compounds. The quaternary ammonium hydroxide-cellulose complexes from either native or mercerized cellulose or their heated modifications

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[127] I. Sakurada and K. Fuchino, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **17**, 294 (1932).

[128] W. Schramek and F. Küttner, *Kolloid-Beihefte*, **42**, 331 (1935).

[129] G. Centola, *Atti X° Congr. intern. Chim.*, **4**, 722 (1939).

[130] H. L. Bredée, *Kolloid-Z.*, **94**, 81 (1941).

[131] A. J. Barry, F. C. Peterson, and A. J. King, paper presented before the Division of Cellulose Chemistry of the Am. Chem. Soc. at Pittsburgh, Sept. 7–11, 1936.

[132] K. Hess and J. Gundermann, *Ber.*, **70B**, 1788 (1937).

[133] K. Hess, and C. Trogus, *Ber.*, **68B**, 1986 (1935).

are entirely reverted to hydrate cellulose by washing with dilute acid and water.

When nitric acid of about 61% reacts with cellulose,[124] a crystalline compound is formed ($2C_6H_{10}O_5:HNO_3$) which gives an x-ray pattern different from native cellulose. Upon washing out the acid the pattern of hydrate cellulose is obtained. Perchloric acid at a limiting concentration of about 9.3 molar forms an addition product with cellulose ($2C_6H_{10}O_5:HClO_4$) which shows a characteristic diagram. Below this concentration only intermicellar swelling occurs as indicated by the native x-ray diagram obtained after washing out the acid; at higher concentrations esterification begins and above 10.6 molar the fiber is destroyed.

Change in X-ray Diagram. When a swelling agent is added to a cellulose fiber the change in x-ray diagram may be divided into three steps, as exemplified by the action of quaternary ammonium hydroxides.[117] When very little base is added, the crystalline pattern is that of the original fiber. At the other extreme, when sufficient base is added, the pattern is that of the swelling compound. Between these two extremes the patterns may indicate the presence of the original unchanged cellulose and of the modified cellulose existing together in the same sample. As the new diagram of the swelling compound is formed, that of the original cellulose loses in intensity. In many cases the sharpness of the swelling compound pattern indicates a crystalline structure as well defined as that of the original cellulose. Likewise, if the fibers are not permitted to shrink during impregnation, the orientation of the swollen fiber may be as good as, or even better than, that of the original fiber. In most cases, there is superimposed upon the crystalline swelling compound pattern an amorphous pattern due to intercrystalline swelling. The intensity of this pattern is proportional to the degree of intercrystalline swelling and the amount of excess reagent present. If the intercrystalline swelling is unlimited, this amorphous pattern may become so intense as to mask the crystalline pattern of the swelling compound completely. This masking effect prohibits further x-ray evidence regarding the effect of excess reagent and the mechanism of the solution process.

Effect of Temperature and Concentration. The formation of a swelling compound is associated with a minimum concentration for each swelling agent, below which only intermicellar swelling occurs and the x-ray diagram of native cellulose is not affected. For some swelling agents, such as sodium hydroxide, the minimum concentration is associated with the temperature, while with others, such as the quaternary ammonium hydroxides, temperature apparently has little effect. As a general rule, low

temperatures assist compound formation. Temperatures may also affect the type of swelling compound formed, as, for example, the formation of a different alkali cellulose at high temperatures[134] and a different ammonia cellulose at low temperatures.[132]

The effect of concentration may be illustrated by alkali cellulose I which is not formed below a sodium hydroxide concentration of approximately 12 to 14% at room temperatures. If the concentration is increased above about 22%, a different compound, alkali cellulose III, is formed. For tetramethyl-, trimethyl-, benzyltrimethyl-, and dibenzyldimethyl-ammonium hydroxides, the limiting concentrations are 16 to 20, 17 to 22, 25 to 29, and 27 to 31%, respectively. These percentages correspond roughly to normalities of 2.0, 1.9, 1.6, and 1.15, which decrease linearly when plotted against increasing molecular weights. In this connection, it is interesting to note that these concentration ranges correspond to the maximum in the curve when equivalent conductivity is plotted against concentration.[73]

The fact that a limiting concentration corresponding to a fairly narrow range is necessary for intramicellar swelling, while intermicellar swelling takes place gradually over a wide concentration range, would appear to be related to the bonding forces between the molecules of the swelling agent and water. In the intercrystalline areas the polar bonds of the hydroxyl groups of cellulose are not mutually satisfied as they are in the crystalline areas. These hydroxyl groups are thus free to compete with those of water in their attraction for the molecules of the swelling agent. Intermicellar swelling may thus begin at low concentrations and increase with higher concentrations. In order to break the cellulose crystallization bonds, on the other hand, it may be necessary for all the water molecules to be used up in forming shells around the swelling agent molecule before excess swelling molecules are free to penetrate the crystal lattice. This mechanism would explain the existence of the various alkali celluloses at different temperatures and concentrations since it is known that the various hydrates between sodium hydroxide and water are a function of temperature and concentration.

Preferential Action. If a mixture of two swelling agents is placed in contact with cellulose, in many cases only one will act as the intramicellar swelling agent. For example, when a mixture containing equivalent amounts of tetramethyl- and dibenzyldimethyl-ammonium hydroxide is applied to cellulose fibers, the tetramethyl molecule exerts the preferential action, since the resulting x-ray diagram shows only the interference pat-

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[134] H. Sobue, H. Kiessig, and K. Hess, *Z. physik. Chem.*, **B43**, 309 (1939).

tern characteristic of the tetramethylammonium hydroxide cellulose complex. This preferential action may be explained by the smaller size of the tetramethyl molecule, but it is probable that polarity may also play a part.

It has been reported[131] that a high-molecular-weight alkyl amine, which is apparently too large to enter the crystal lattice alone, may be made to enter by first swelling the lattice with a lower amine. This substitution is assisted by a higher concentration of the larger amine and a longer reaction time.

Lattice Extension. When one compares the lattice spacings of a swelling compound with those of the original cellulose it is obvious that the most striking change occurs in the distance between the (101) planes. From a minimum of 6.1 Å. in native cellulose, this equatorial interplanar distance increases to a maximum of approximately 16.7 Å. for the dibenzyldimethylammonium hydroxide cellulose compound. This expansion apparently allows room for the introduction of the swelling reagent into the unit cell. The 101 interplanar spacings for several swelling compounds are listed in Table 3.

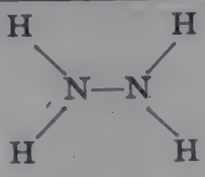
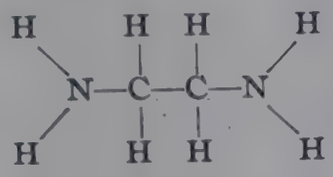
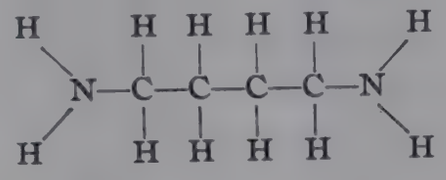
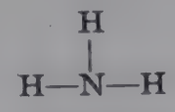
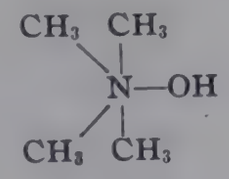
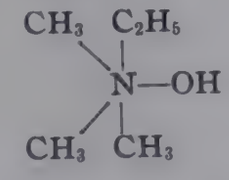
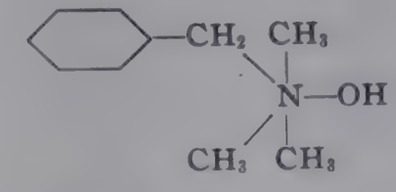
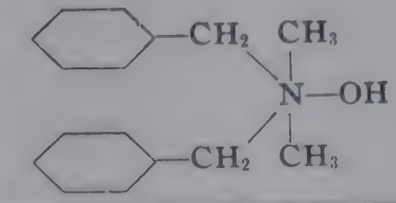
In the diamines[116] the increase in the 101 interplanar spacing is proportional to the length of the diamine molecule, and with the alkyl amines the spacing is directly related to the size of the alkyl group of the entering molecule.[131] With the quaternary ammonium hydroxides,[117] however, the increase is not always directly proportional to the size of the substituted groups as, for example, when a methyl group is replaced by an ethyl group, or when the organic base contains two benzyl groups instead of one. These results may be explained by assuming that the molecules of the swelling agent have a definite orientation in the crystal lattice, and that the polar group is oriented in the direction of, and forms secondary valence bonds with, the hydroxyl groups of the cellulose chain. Thus, in the amines where the polar groups are at the end of the molecule and the increase in molecular weight consists of an increase in chain length, the 101 interplanar spacing is proportional to the molecular size. In the quaternary ammonium hydroxides, the second benzyl group, for example, does not appreciably increase that dimension of the molecule which arranges itself perpendicular to the (101) plane of the cellulose unit cell. For the smaller molecules such as sodium hydroxide the same explanation apparently holds, but here the molecules of the swelling agent may assume various arrangements in the unit cell to give several soda celluloses.

From the above discussion it is obvious that during swelling compound formation the cellulose chains in their lateral expansion behave as though they had a laminated structure, since the unit cell expands in only one di-

rection. This expansion of the unit cell in the direction perpendicular to the (101) plane only is probably due to the directional distribution of the secondary valence forces between the cellulose chains. Apparently, the

TABLE 3

EFFECT OF SEVERAL SWELLING AGENTS ON THE 101 INTERPLANAR SPACING OF CELLULOSE

Swelling compound	Formula	Observed 101 spacing in Å.
Hydrazine		10.3
Ethylenediamine		12.26
Tetramethylenediamine		14.65
Liquid ammonia		10.3
Tetramethylammonium hydroxide		13.0
Ethyltrimethylammonium hydroxide		13.0
Benzyltrimethylammonium hydroxide		16.5
Dibenzyldimethylammonium hydroxide		16.5

first action of an intracrystalline swelling agent is to break those hydrogen bonds between the cellulose chains which exist along the *ab* plane of the unit cell (see Fig. 5). If the swelling agent has only one polar group which forms a bond with the hydroxyl of the cellulose chain, then the plane of the glucose unit rotates approximately 30° and forms bonds with its next neighbor in the center of the unit cell. This shifts the plane of the glucose residues from the *ab* plane to a plane bisecting the *ab* and *cb* planes so that the hydroxyl groups now lie in the 101 plane. The plane containing the van der Waals' forces is thus shifted from the 002 to the $10\bar{1}$ crystallographic plane. These van der Waals' forces are little disturbed by the entrance of the swelling agent and as a result the $10\bar{1}$ interplanar distance is not a function of the molecular size of the swelling agent. The main valence chains are held together along the (101) plane by bonds formed through the swelling agent, and as a result the 101 interplanar distance is a function of the molecular size of the swelling agent. This mechanism of swelling would explain why a swelling agent which has only one hydrogen bonding atom gives the hydrate unit cell structure upon removing the swelling agent, while those containing two hydrogen bonding atoms at each end of the swelling molecule (*e. g.*, diamines) hold the plane of the glucose unit in the *ab* plane of the unit cell and thus assist the bonds between the glucose units to reunite in a manner characteristic of the native structure when the swelling agent is removed.

(*d*) *Mercerization*

Technically, the most important of swelling phenomena is the action of sodium hydroxide on cellulose, known as mercerization. The name is derived from the fact that John Mercer in 1844 observed that if cotton, either in the form of yarn or fabric, was treated with strong sodium hydroxide, it suffered considerable shrinkage, and that its tensile strength, chemical reactivity, and dye absorption increased. Modern textile mercerization is associated with increased luster and tensile strength obtained by treating cotton under tension. The mercerizing effect may be obtained also by other alkali hydroxides, organic bases, certain salt solutions, liquid ammonia, and strong acids. In the viscose rayon industry, the term mercerization has a specialized meaning, in that it refers only to the aging of alkali cellulose, but in the textile industry mercerization usually refers to the physical aspects of the process and the resulting product. A comprehensive discussion of mercerization may be found in a recent book by Marsh.[135] The

[135] J. T. Marsh, *Mercerising*. Chapman & Hall, London, 1941.

present discussion will be limited to the swelling action of sodium hydroxide on cellulose fibers and to the formation of alkali cellulose.

When sodium hydroxide of less than about 12% reacts with cellulose fibers at room temperature there is no change in the crystal lattice, and one is forced to conclude that the swelling below this concentration is of the intermicellar type. With increasing concentration or decreasing temperature, however, the change in the lattice shows that an intramicellar change has taken place, and it must be assumed that the interior of the crystalline cellulose has now become accessible to the alkali. It is interesting to note that the point where intramicellar swelling begins coincides with the temperature and concentration at which maximum water absorption occurs, and the point corresponds to the break in Vieweg's absorption curve.

Much work has been done on the question of whether sodium hydroxide forms a compound with or is merely absorbed by cellulose. Mercer's original observation that cotton removed alkali from solution led him to believe that a chemical combination took place, followed by decomposition of the compound on treatment with water in a manner similar to the formation of sodium ethoxide and its subsequent hydrolysis. Furthermore, it is difficult to account for the viscose reaction without assuming an alcoholate formation between cellulose and sodium hydroxide. Gladstone[136] removed the uncombined alkali from cotton by washing, with alcohol, and found the compound $(C_6H_{10}O_5)_2 \cdot NaOH$. Vieweg[137] made the first quantitative measurements of the absorption of sodium hydroxide from solution and found two breaks in the curve corresponding to the compounds $(C_6H_{10}O_5)_2 \cdot NaOH$ and $(C_6H_{10}O_5)_2 \cdot 2NaOH$. Since then many workers have measured the absorption of sodium hydroxide by various techniques. Some have found evidence for compound formation while others have not. Excellent reviews of these researches may be found in the literature.[138, 139, 140] In the light of our present knowledge of swelling and cellulose structure, it is now quite certain that during mercerization both absorption and compound formation take place and that the complex phenomenon is associated with the amorphous and crystalline structure of the cellulose fiber as evidenced by x-ray analysis.

The x-ray examination of mercerization has been of two types: (1) x-ray

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[136] J. H. Gladstone, *J. Chem. Soc.*, **5**, 17 (1852).

[137] W. Vieweg, *Ber.*, **40**, 3876 (1907).

[138] D. A. Clibbens, *J. Textile Inst.*, **14**, T217 (1923).

[139] W. D. Bancroft and J. B. Calkin, *Textile Research*, **4**, 119, 159 (1934).

[140] J. T. Marsh and F. C. Wood, *An Introduction to the Chemistry of Cellulose*. Chapman & Hall, London, 1938.

diagrams obtained when the alkali is left in the fibers, and (2) examinatio of the fibers after removal of the alkali. When one examines cotton afte removal of the alkali, three general types of x-ray diffraction patterns ar obtained showing either (1) native cellulose, (2) or completely mercerize cellulose, or (3) both native and mercerized cellulose.

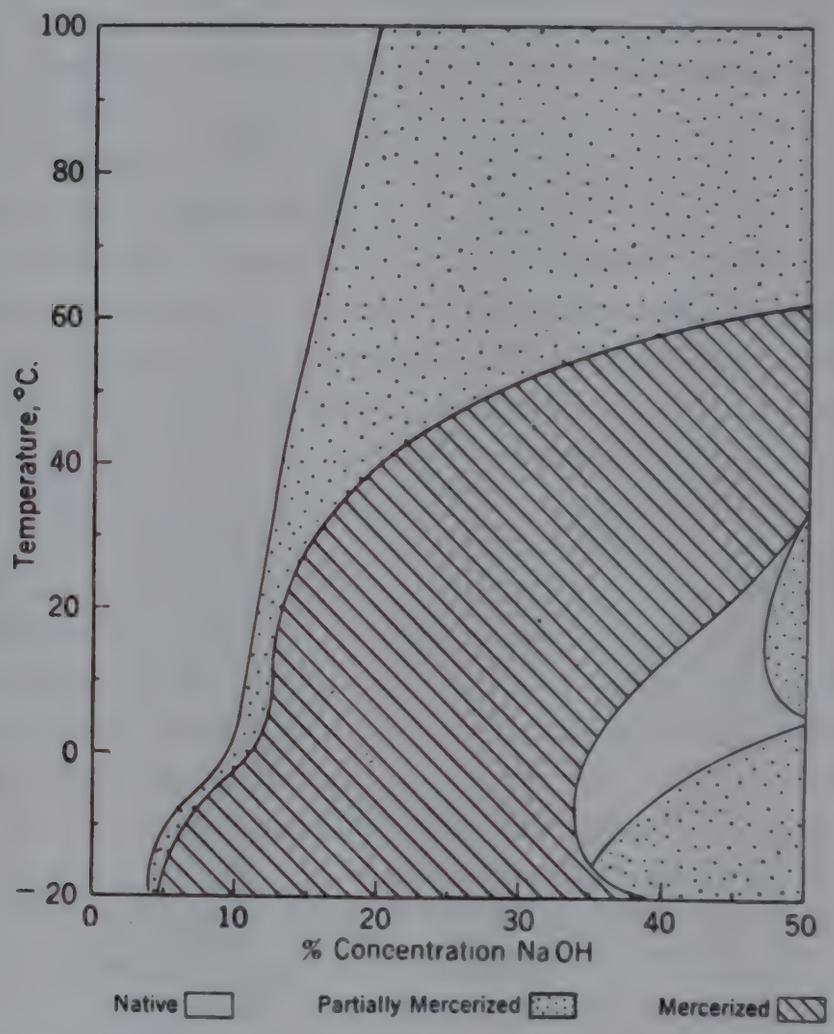

FIG. 26.—GRAPHICAL REPRESENTATION OF THE EFFECT OF TREATING RAW COTTON WITH SODIUM HYDROXIDE AT VARIOUS TEMPERATURES AND CONCENTRATIONS (SISSON AND SANER[141]).

The effect of temperature and concentration on the type of x-ray patterns obtained for raw cotton[141] after treatment with alkali is shown in Figure 26. Upon examining Figure 26, it is apparent that complete mercerization is obtained at room temperature (20°C.) when the concentration of sodium hydroxide is above 13 to 14%. As the temperature is lowered, the concentration required for complete mercerization becomes in-

[141] W. A. Sisson and W. R. Saner, *J. Phys. Chem.*, **45**, 717 (1941).

creasingly lower until, with 5% sodium hydroxide, complete mercerization is not obtained until the temperature has been lowered to about −18°C. With 3% sodium hydroxide there is no indication of mercerization with temperatures as low as −70°C. Mercerization below the freezing point of dilute sodium hydroxide solutions (3 to 13%) probably depends on the fact that ice separates out leaving behind more concentrated solutions of sodium hydroxide which are capable of mercerization.

Partial Mercerization. Preceding complete mercerization there is a certain concentration range which gives only partial mercerization. This concentration range is rather narrow between −20° and +30°C., but becomes quite extensive at higher temperatures, until at about 65°C. it extends from approximately 16 to 50% sodium hydroxide.

At low temperatures (−20° to +30°C.) and high concentrations (35 to 50% sodium hydroxide) the area of complete mercerization is interrupted by another area of partial mercerization. The lack of complete mercerization in this area is probably due to the formation of sodium hydroxide hydrates at these concentrations which are incapable of penetration into the crystalline cellulose lattice.

Cotton fibers containing only partially mercerized cellulose appear to be of great commercial importance, since most commercially mercerized yarns and fabrics show a mixture of native and mercerized cellulose when examined with x-rays. The variation in relative amounts of native and mercerized cellulose may be partially responsible for the variation in properties obtained by specialized commercial mercerization treatments. The ratio of native to mercerized cellulose obtained after mercerization is affected by the temperature and concentration of the mercerizing bath, the previous treatment (degradation) of the fiber, and by the presence of tension or compression on the fibers during mercerization.

At room temperature raw cotton is completely mercerized with 18% sodium hydroxide, but upon heating the mercerizing and washing bath to a higher temperature the structure is partially reverted to the native form. Thus, a mixed pattern may be obtained either from cotton treated with 18% sodium hydroxide at temperatures above 65°C., or from cotton treated first with cold 18% sodium hydroxide and then heated, either by raising the temperature of the mercerizing bath or by removing the sample from cold alkali and plunging it into boiling water. Complete mercerization, however, is obtained if the sample treated at room temperature is first washed in cold water and then plunged into boiling water, or if a sample treated above 65°C. is plunged into ice water. The apparent effect of plunging the sample into either hot or cold water is to change the tempera-

ture of the sodium hydroxide-impregnated fiber before the sodium hydroxide within the fiber is diluted to a concentration beyond which a reaction typical of the new temperature cannot take place.

X-ray studies show that the native pattern is changed to the mercerized form within a few seconds upon treatment with 18% sodium hydroxide at room temperatures. Above about 75°C. a partially mercerized pattern is obtained which gradually changes to complete mercerization after heating for days. This gradual change could be due to a slow mercerization reaction, but it appears more probable that the intracrystalline swelling attains equilibrium in a short time and that the effect of prolonged action is due to degradation. Fibers treated in the absence of oxygen with 25% NaOH at 75°C. still show partial mercerization after 15 days' treatment.

The x-ray diagram of cotton partially mercerized at room temperature indicates that the native and the mercerized cellulose exist as two separate crystalline phases. In samples which have been partially reverted at high temperatures, however, there is less definite indication of two distinctly separate crystalline phases. The two inner lines of the native x-ray pattern are not clearly resolved, which would indicate the possibility of a mixed crystallization. Partial mercerization appears to be connected in some way with fiber structure since cotton fibers cut into short sections show less partial mercerization while those ground to a fine powder show only complete mercerization.

Effect of Degradation. When cotton fibers are oxidized or hydrolyzed with acids, the area of partial mercerization is gradually decreased as degradation proceeds[141] (see Fig. 27). Furthermore, degraded fibers are more highly swollen after treatment with sodium hydroxide, especially at low temperatures and concentrations. X-ray and microscopic studies indicate that the increased swelling is largely of the intermicellar type since the degraded fibers still give the same alkali cellulose diagram as the original fibers. This increased intermicellar swelling as a result of degradation leads to dispersion in sodium hydroxide solution, which is greatest at a concentration of approximately 10% and a temperature near the freezing point.

Since degradation apparently changes the limited intermicellar swelling to the unlimited type, without affecting the nature of the intramicellar swelling, one would expect sodium hydroxide solutions of degraded cotton to consist largely of gel particles suspended in a complete molecular dispersion of degraded cellulose. This would be in keeping with the fact that weak films and fibers are always obtained with cellulose regenerated from sodium hydroxide solution, the low-viscosity continuous phase having low inherent strength. In rayons, the solubility in sodium hydroxide is ap-

parently associated with the fiber structure since the ratio of crystalline to amorphous cellulose appears to be of greater importance than the average degree of polymerization.

The effect of tension on mercerization has been pointed out by Hess and Trogus.[142] Their experiments, which have been repeated with both sodium

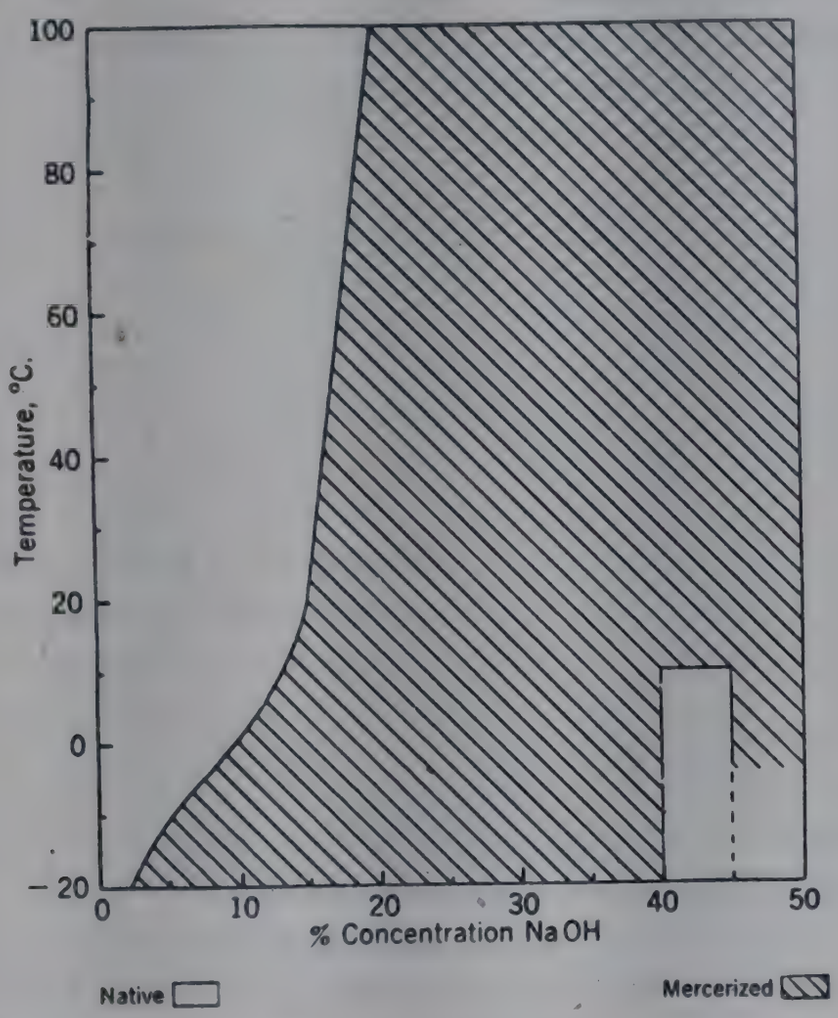

FIG. 27.—GRAPHICAL REPRESENTATION OF THE RESULTS OBTAINED WITH KIERED AND BLEACHED COTTON PRETREATED WITH 1 *N* HCl FOR 4 HOURS AT 75°C. BEFORE TREATMENT WITH SODIUM HYDROXIDE AT VARIOUS TEMPERATURES AND CONCENTRATIONS (SISSON AND SANER[141]).

Area in lower-right-hand corner not investigated.

hydroxide and quaternary ammonium hydroxides by the author, show that intramicellar swelling may be partially prohibited by keeping the fibers under tension during the immersion in alkali, or by stretching the fibers before and during the washing out of the sodium hydroxide. When the fibers are held under tension it may be necessary to use 30 to 35% NaOH to obtain the mercerized diagram as compared with 13% in the case of un-

[142] K. Hess and C. Trogus, *Z. physik. Chem.*, **B4**, 321 (1929); **B11**, 381 (1931).

stretched fibers, and, if sufficient tension is applied, the application of 45% NaOH for a week still gives the diagram of native cellulose if the sample is washed under tension. These and other experimental trials on the increased swelling of rubbed fibers[143] all point to the fact that any restrictive action, produced either by external forces or by the cuticle, tends to prohibit complete mercerization.

Alkali Cellulose. A great many of the investigations regarding the structure and formation of the alkali celluloses has been carried out by Hess and coworkers[134, 142, 144, 145] who examined the x-ray diagrams obtained when sodium hydroxide and other alkalies are left in the cellulose fibers. At room temperatures several soda celluloses are formed, depending upon the concentration of the alkali solution. Between a concentration of about 12 and 19% NaOH, the so-called soda cellulose I is formed which gives a definite x-ray pattern. When this is dried a further diagram is obtained of a product designated as soda cellulose III, which reverts to soda cellulose I when treated with water. Above a concentration of about 21% another diagram corresponding to a product called soda cellulose II is obtained. This does not change upon dehydration, but when sufficient water is added soda cellulose I is formed. The transition from one diagram to another does not occur sharply and mixed diagrams are obtained over a range. More recently[134] the effect of temperature and concentration has been worked out and there are indications of at least five soda celluloses. It has been emphasized[142] that water is necessary for the formation of soda cellulose I, and for the rearrangement of soda cellulose II to soda cellulose I. It has also been observed[145] that soda cellulose I, when washed with water at 100°C. and dried, gives the diagram of both native and mercerized cellulose. From the data which have been published[134] on the increased volume of the unit cell of soda celluloses I and II, it appears likely that water, as well as sodium hydroxide, enters the unit cell to form the swelling compounds. Additional information on alkali cellulose is given in Chapter VIII, D.

Most of the phenomena associated with the formation of other swelling compounds appear to hold for the formation of alkali cellulose. For example, the hydroxyl groups of the glucose units rotate into the (101) plane and the crystal lattice expands perpendicular to the (101) plane so that the cellulose chains act as lamellae in their expansion to allow room for the entrance of the sodium hydroxide and water. The intramicellar swelling

[143] M. A. Calvert, *J. Textile Inst.*, **21**, T293 (1930).
[144] C. Trogus and K. Hess, *Z. Elektrochem.*, **42**, 704 (1936).
[145] K. Hess and J. Gundermann, *Ber.*, **70B**, 527 (1937).

associated with the formation of alkali cellulose is strictly of the limited type and only when treated with a further reagent such as carbon disulfide does the swelling become unlimited.

Mechanism of Mercerization. As pointed out in the earlier discussion on fiber structure, x-ray and microscopic data both indicate the presence of a dual structure in a native cellulose fiber. The fiber is built up of crystalline fibrils which are separated by amorphous interfibril material. It seems logical, therefore, to assume that the over-all action of the sodium hydroxide must be considered upon the basis of its specific action upon the separate components of the fiber.

X-ray and microscopic observations made throughout the mercerization process indicate that the crystalline phase and the amorphous phase each are affected by the sodium hydroxide in a different manner.[141] X-ray diagrams show that when cotton fibers are swollen with sodium hydroxide the original native crystalline cellulose pattern disappears and that a new crystalline pattern (soda cellulose) is obtained which is characteristic of a swelling compound. At the same time, the original weak amorphous pattern is displaced by a new amorphous pattern, which is now so intense as almost to cover up the crystalline pattern. If the fibers are washed with water and dried, the pronounced amorphous pattern decreases and the crystalline pattern of the swelling compound is displaced by the pattern of mercerized cellulose. Microscopic observations in both ordinary and polarized light show that in sodium hydroxide the increase in fiber diameter is largely due to swelling of the hydrophilic interfibril material. This swelling pushes the fibrils apart and partially disarranges their original orientation with the result that the fiber increases in diameter and decreases in length, since the fibril itself is only slightly swollen but not disrupted by the treatment with sodium hydroxide.

If one considers a cellulose fiber as a two-phase system (crystalline and intercrystalline material), then it is possible to think of mercerization as a twofold reaction: (a) soda cellulose or swelling compound formation (intramicellar swelling) by the crystalline phase, and (b) alkali absorption (intermicellar swelling) by the intercrystalline or amorphous phase.

This suggested dual mechanism of mercerization would explain the lack of a true equilibrium in the system cellulose-sodium hydroxide[146] and serve as a compromise in the long-debated question as to whether cotton fibers take up sodium hydroxide by sorption or by compound formation.[140] The form of the cotton-alkali absorption curve would be in agreement with the x-ray and microscopic data, which indicate that most of the fiber swelling

[146] W. Schramek and H. Görg, *Kolloid-Beihefte*, **42**, 302 (1935).

and sorption of solution is due to the pronounced swelling of the intercrystalline material. Likewise, the chemical evidence regarding compound formation is in agreement with the x-ray data, which indicate the formation of a definite swelling compound between sodium hydroxide and the crystalline cellulose at the concentration corresponding to the break in the absorption curve. The chemical reaction corresponding to alcoholate formation thus occurs in both the amorphous and crystalline areas, but with greater ease in the amorphous areas where swelling beyond soda cellulose formation occurs. On the basis of swelling experiments, Neale[147] has made a somewhat similar suggestion that the behavior of cellulose in sodium hydroxide solution can be explained on the assumption that alkali is taken up (1) according to the law of mass action to form a sodium salt, and (2) without chemical reaction in amount necessary to satisfy the Donnan equation of membrane equilibrium.

(*e*) *Hydration*

The general term hydration, as used in the literature, may refer to any of a large number of phenomena concerned with the taking up of water, the specific reference depending upon the particular phase of cellulose chemistry under discussion. The present discussion on hydration will be limited to x-ray data regarding the formation and properties of hydrate cellulose.

Swelling compounds, as a general rule, are easily decomposed by water. Upon removal of the swelling agent the fiber shrinks in diameter, and, after drying, the x-ray diagram shows the presence of a crystalline structure which differs from that of the original fiber. This regenerated structure is known as the hydrate or mercerized form, and as discussed earlier (see Fig. 5) it differs crystallographically from the native form in that the glucose residues are rotated approximately 30° around the main valence chain axes to form new interchain bonds and new interplanar distances. Hydrate cellulose has the same organic chemical structure as native cellulose but it is more reactive. This increased reactivity may be explained, partly by the geometrical arrangement of the glucose units which are farther apart and are oriented in the crystal lattice so as to make the hydroxyl groups more available, and partly by the greater proportion of amorphous areas created by the swelling or solution process which must precede the formation of a hydrate structure.

Earlier workers considered sodium hydroxide to form a chemical compound with cellulose which was decomposed by the action of water in the

[147] S. M. Neale, *J. Textile Inst.*, **20**, T373 (1929)

same manner as other alcoholates. This view gave use to the term "cellulose hydrate" and "hydrated cellulose." It was assumed that the mercerized product differed from the native by the presence of water in hydrate combination, which accounted for the difference in properties.[140] The name still persists but its meaning has been modified since it is now known that hydrate cellulose has the same analytical composition as the native form and is free from water.

Cellulose regenerated from its solutions have been classified[148] as either the "hydrate cellulose" or the "hydro-oxycellulose" form. The hydrate cellulose has the expanded lattice typical of cellulose which has undergone intracrystalline swelling, while the hydro-oxycellulose has the original native cellulose lattice. It is probable that the latter, as a result of intercrystalline degradation, has undergone only unlimited intermicellar swelling to give a colloidal rather than a molecular solution.

Hydrate, mercerized, dispersed, and regenerated cellulose all have essentially the same crystalline x-ray diagram with the exception of slight differences in relative line intensities. Conversely, it might be said that the presence of a hydrate diagram is always indicative that the cellulose has been subjected either to intramicellar swelling or to derivative formation.

Water Cellulose. Sakurada with Fuchino[149, 150] and Okamura[151] has shown that when a swelling compound, such as alkali cellulose, is washed with water until free from alkali, and then examined in the wet state, it gives a new and fairly sharp x-ray diagram. This diagram indicates a lattice which is less distended than that of the alkali cellulose but still more distended than that of the mercerized or hydrated lattice, which is the final dried form. This new x-ray diagram indicates that the sodium hydroxide of the alkali cellulose has been displaced by water which now occupies a definite position in the crystal lattice of the cellulose. This swollen modification, which is a true hydrate cellulose, is designated as "water cellulose."

Water cellulose is stable indefinitely if kept in water at room temperature. It is also stable toward mineral acids. If dried in air it is changed to hydrate cellulose, slowly at low temperatures, but faster at higher temperatures. If alkali cellulose is washed with hot water, or if water cellulose

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[148] S. E. Sheppard, *J. Phys. Chem.*, **34**, 1052 (1930).

[149] I. Sakurada and K. Fuchino, *Kolloid-Z.*, **77**, 346 (1936).

[150] I. Sakurada and K. Fuchino, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **14**, 171 (1935).

[151] I. Sakurada and S. Okamura, *J. Soc. Chem. Ind., Japan*, **41**, suppl. binding, 70 (1938).

is heated in water, the hydrate lattice is formed. After the hydrate lattice is once formed it is not reversible to the water cellulose form by the addition of water. The only way in which water cellulose can be formed again is to go through the cycle of forming a swelling compound followed by washing with water.

Water cellulose has been obtained from cellulose swollen in all of the alkali hydroxides, from cellulose xanthate, and also from cellulose regenerated from cuprammonium hydroxide and sulfuric acid solutions. Water cellulose will hold about twice as much total absorbed water as hydrate cellulose when centrifuged, and it is more reactive chemically. The lattice constants of water cellulose as compared with those of native, alkali, and hydrate cellulose are given below.

Axis	Native cellulose	Alkali cellulose	Water cellulose	Hydrate cellulose
a	8.35 Å.	12.8 Å.	10.03 Å.	8.1 Å.
b	10.3 Å.	10.3 Å.	10.3 Å.	10.3 Å.
c	7.9 Å.	13.2 Å.	9.98 Å.	9.1 Å.
β	84°	40°	52°	62°

The expanded lattice of water cellulose may be utilized to retain in part the increased reactivity associated with alkali cellulose, especially for reactions which must be carried out in a neutral or acid solution. It is also possible to keep the lattice expanded by washing out the sodium hydroxide with alcohol. In this case, however, the sodium hydroxide is not completely removed. The dried product gives a definite x-ray diagram, showing an expanded lattice, and chemical analysis shows the presence of both ethoxyl groups and sodium in fairly definite proportions. Washing with water removes the sodium and ethyl groups and the dried product shows the pattern of hydrate cellulose.

Conversion of Hydrate to Native Cellulose. It was first shown by Meyer and Badenhuizen[152] and later confirmed by Kubo[153, 154, 155] that when strongly stretched hydrated cellulose (Lilienfeld rayon) is heated 30 min. at 200°C. in water or formamide, it is partly changed into native cellulose as shown by x-ray diffraction patterns. The pattern of both native and hydrate is present, and heating in water for eight days formed very little more native cellulose than is formed in 30 min. Viscose rayon heated

[152] K. H. Meyer and N. P. Badenhuizen, *Nature*, **140**, 281 (1937).
[153] T. Kubo and K. Kanamaru, *Z. physik Chem.*, **A182**, 341 (1938).
[154] T. Kubo, *Kolloid-Z.*, **88**, 62 (1939).
[155] T. Kubo, *Cellulose Ind. (Tokyo)*, **15**, 99 (1939).

in glycerol at 250°C. for 30 min. gave almost complete conversion to the native form. This reversion is concerned only with the crystalline structure and has no relation to the fiber or morphological structure. When hydrate cellulose obtained by the mercerization of cotton is treated under similar conditions, less native cellulose is formed from this material than from rayon. Dry rayon heated for 20 min. at 200°C. in a high vacuum remains unchanged, but after 10 min. at 300°C. a little native cellulose is formed. This indicates that water and other dipole liquids facilitate the transformation.

The effect of heating cellulose with a large number of materials in both the liquid and gaseous state has been studied by Kubo[153] who found that the degree of transformation increases proportional to the polarity of the liquid used. If hydrate cellulose is first swollen with sodium, potassium, or lithium hydroxide[154] or with one of the diamines,[155] the transformation to the native form is greatly facilitated, allowing almost complete conversion. The difference is ascribed to the separation of the cellulose chains by the swelling agent which permits freer relative rotation of the glucose units back to the native form. Conversion to the native form is said to increase the fiber orientation.

Partial conversion may result from heating alkali cellulose as shown by the fact that a small amount of native cellulose is formed when alkali cellulose is washed with water at 100°C. If, however, washing takes place with water first at 20°C. followed by heating, no native cellulose appears even at 100°C. It is also possible to obtain native cellulose from hydrate cellulose by way of the ammonia cellulose compound[122] which gives the pattern of native cellulose when decomposed with weak acetic acid, water, or aqueous ammonia.

Since native cellulose remains unchanged upon heating, Meyer[152] has suggested that native cellulose is the stable form and hydrate cellulose the unstable form at high temperatures. It is impossible to decide from these data which is the stable form at room temperature. It is not known why fibers during growth should deposit cellulose in an unstable native crystalline state, or as to why the marine alga, *Halicystis*, should deposit the stable hydrate form.[67]

Cellulose Derivatives. Whenever derivatives of cellulose are hydrolyzed, the x-ray diagram of the resulting product is usually that of hydrate cellulose.[111] For example, cellulose regenerated by the saponification of cellulose acetate gives the spectrograph of mercerized cellulose. The process is reversible and the cellulose is changed into the mercerized form each time that it undergoes acetylation followed by saponification.

Certain of the acetates and nitrates, however, give x-ray diagrams which present unhomogeneous materials, and after hydrolysis the products show the superposition of interferences of natural cellulose and mercerized cellulose. Cellulose fibers obtained by the denitration of nitrocellulose and from the hydrolysis of cellulose acetate (prepared from unmercerized cellulose) give diagrams of native cellulose, while cellulose regenerated from esters prepared from mercerized cotton gives diagrams of cellulose hydrate.

Since denitrated cellulose may be composed of micelles of both lattices, it has been suggested that the transition of cellulose from the native to the mercerized lattice does not occur in nitration, but during hydrolysis. It is also thought that the denitration of a trinitrocellulose fiber proceeds in a micellar heterogeneous manner, since the denitration product may contain unchanged material in the interior of the micelle. Hydrolysis of acetates containing both the crystalline and amorphous phase causes the disappearance of the crystalline part first, which is doubtless the triacetate. Cellulose which has been cautiously nitrated (13.5% nitrogen) and then denitrated by ammonium sulfide gives only a moderately strong line and thus appears amorphous; when dissolved in cuprammonium solution and reprecipitated, it shows a definite x-ray diagram of cellulose hydrate. Likewise, when deacetylation is carried out in a nonaqueous medium (ethanol-sodium hydroxide solution), an indefinite or amorphous pattern is obtained which is changed to a well-defined crystalline cellulose hydrate pattern when the sample is treated with water.

Amorphous Hydrate Cellulose. A product which fails to give a characteristic, crystalline pattern may be obtained by removing an intracrystalline swelling agent with a solvent less polar than water. For example, if soda cellulose is washed with acetone or chloroform, instead of water, the dried product gives a diffraction pattern in which the 101 line is weak and the $10\bar{1}$ and 002 exist only as broad diffuse bands. If the material, however, is thoroughly washed in water and dried, it then gives a typical hydrate pattern.

A logical explanation of this phenomenon would appear to be possible on the basis of the polarity of the cellulose hydroxyl groups and the polarity of the washing liquid. As previously pointed out, when sodium hydroxide produces intracrystalline swelling, the chains are extended laterally only in a direction perpendicular to the (101) plane, with the hydroxyl groups occupying the 101 interplanar space. Upon washing with water, the sodium hydroxide molecules in the lattice are displaced by water molecules, which being highly polar, still hold the hydroxyl groups of the glucose units perpendicular to the (101) plane. As the water leaves the

lattice upon drying, the cellulose hydroxyl groups are thus oriented in a position to form crystalline, interchain polar or hydrogen bonds which are characteristic of hydrate cellulose. If, on the other hand, the water of water cellulose is displaced by a less polar liquid, then there is no guiding force to align the glucose units as they approach each other upon drying. As a result, the long axes of the cellulose chain may still be parallel, but the glucose units have lost their regularity of orientation in three dimensions which is necessary to satisfy the x-ray definition of crystallinity.

B. STRUCTURE OF WOOD

GEORGE J. RITTER

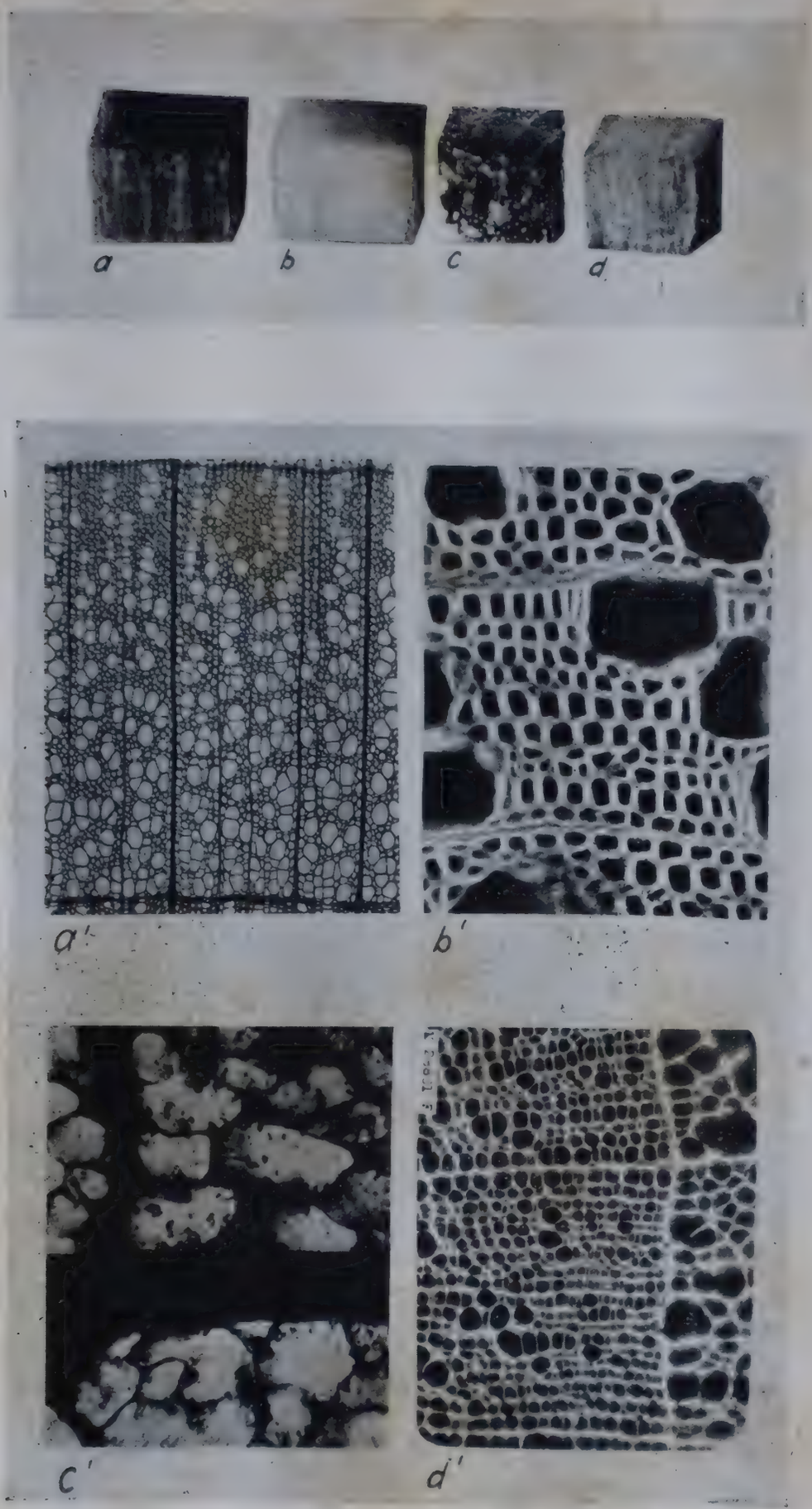
Wood is an excellent source of structural material and of cellulose fibers intended for the manufacture of paper and cellulose derivatives. It is light, easily sawed, cut, planed, shaped, steamed, bent, plasticized, molded, fabricated, and assembled by means of nails, screws, or glues. It responds to these treatments readily and, as a result, an artisan with simple tools can fabricate and assemble it, on the job, into complex structures without the employment of intricate equipment. Wood is also an efficient insulator for heat, sound, and electricity, which is of prime importance in structural material. These desirable properties of wood are due in a large measure to its structure.

Wood is extremely porous. An idea of its porous nature is obtainable without a microscopical examination. For example, the average specific gravity of dry blocks of wood from a large majority of the species is approximately 0.5, whereas that of the dry wood substance is approximately 1.5. Thus the ratio of the two specific gravities indicates that about two-thirds of any wood specimen is composed of air cavities. Immersion of the dry specimens into boiling water displaces the air and causes the wood specimens to sink.

The cavities in which air accumulates, when water is removed from wood during drying, are known as the lumina of the various cells and as intercellular spaces, which are formed at the junction of three or more cells. These cavities form the gross capillary system of wood and are the reservoirs for free water in water-soaked wood.

A potential fine capillary system also is found in wood. It exists between the cellulose aggregates which consist of crystalline and amorphous cellulose particles. This capillary system is potential in that it is reduced to approximately zero when wood is dried, but it readily increases to approximately 45% of the dry solid-wood substance when the material adsorbs enough moisture to reach fiber saturation. This system is, therefore, responsible for the swelling and shrinking of wood during the sorption of moisture.

Wood is composed of a small fraction (1.0%) of ash-forming minerals, 18 to 27% of lignin, and 70 to 80% of holocellulose, which consists of alpha-



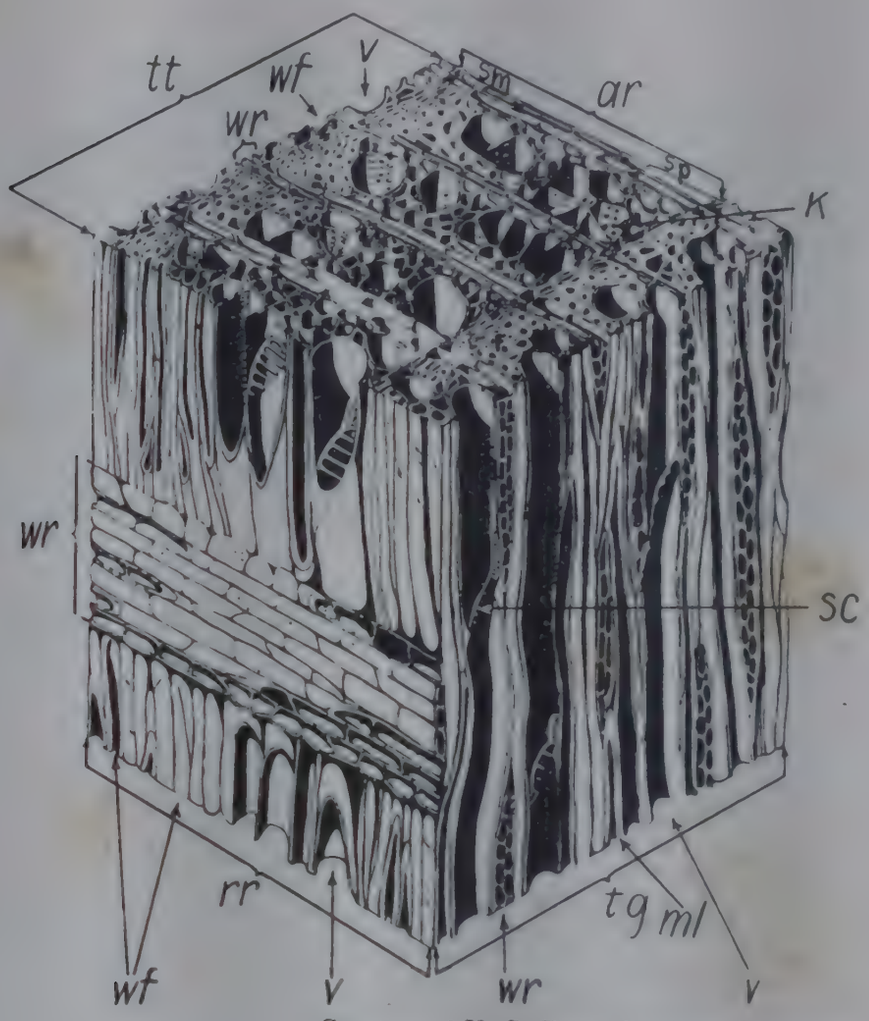
Courtesy of U. S. Forest Products Laboratory

FIG. 28.—BLOCKS OF WOOD AND SOME OF ITS FRACTIONS.

a. Small block of wood, 3 mm. on edge.
a'. Cross section of wood, *a*.
b. Holocellulose from *a*.
b'. Cross section of holocellulose, *b*.
c. Lignin from *a*.
c'. Cross section of lignin, *c*.
d. Ash residue from *a*.
d'. Cross section of ash residue, *d*.

Magnification of: *a'*, × 20 diam.; *b'*, × 100 diam.; *c'*, × 200 diam.; *d'*, × 50 diam.

cellulose and the hemicelluloses. These three fractions make up the wood structure which is infiltrated with water-soluble and ether-soluble substances. The minerals, the lignin, and the holocellulose are well distributed throughout the wood structure. In fact, they are so uniformly



Courtesy of U. S. Forest Products Laboratory

FIG. 29.—DIAGRAM OF BLOCK OF HARDWOOD.

tt.	Transverse surface.	*sm.*	Summerwood.
rr.	Radial surface.	*ar.*	Annual ring.
tg.	Tangential surface.	*k.*	Vessel pit.
wf.	Wood fiber.	*wr.*	Wood ray.
v.	Vessel.	*ml.*	Middle lamella.
sp.	Springwood.		

Magnification × 55 diam.

interspersed that any one of them alone forms a microstructural pattern of the wood. This can be demonstrated by small wood blocks approximately 3 mm. on edge which have been freed of their infiltrated substances and are shown in Figure 28.

Specimen *a* in Figure 28 is a photograph of a block of wood freed of its

infiltrated materials. Specimen *b* is the holocellulose residue from a duplicate of specimen *a;* it was prepared by removing the lignin by means of alternate treatments with chlorine and alcohol-monoethanolamine solution. Specimen *c* is the lignin residue from a duplicate of specimen *a;* it was prepared by removing the holocellulose by means of sulfuric acid. Specimen *d* is the ash residue obtained by burning all the organic material in a duplicate of specimen *a;* it is equivalent to 0.5%, by weight, of the dry wood. It is exceedingly porous and light on account of the high proportion of air cavities in respect to the solids.

Specimen *a'* is a cross section of the wood and shows the structure of the upper face of specimen *a* when observed microscopically. Specimen *b'* shows the microstructure of the upper face of the holocellulose specimen *b*. Specimen *c'* shows the microstructure of the upper face of the lignin specimen *c*. Specimen *d'* shows the microstructure of the upper face of the ash-residue specimen *d*.

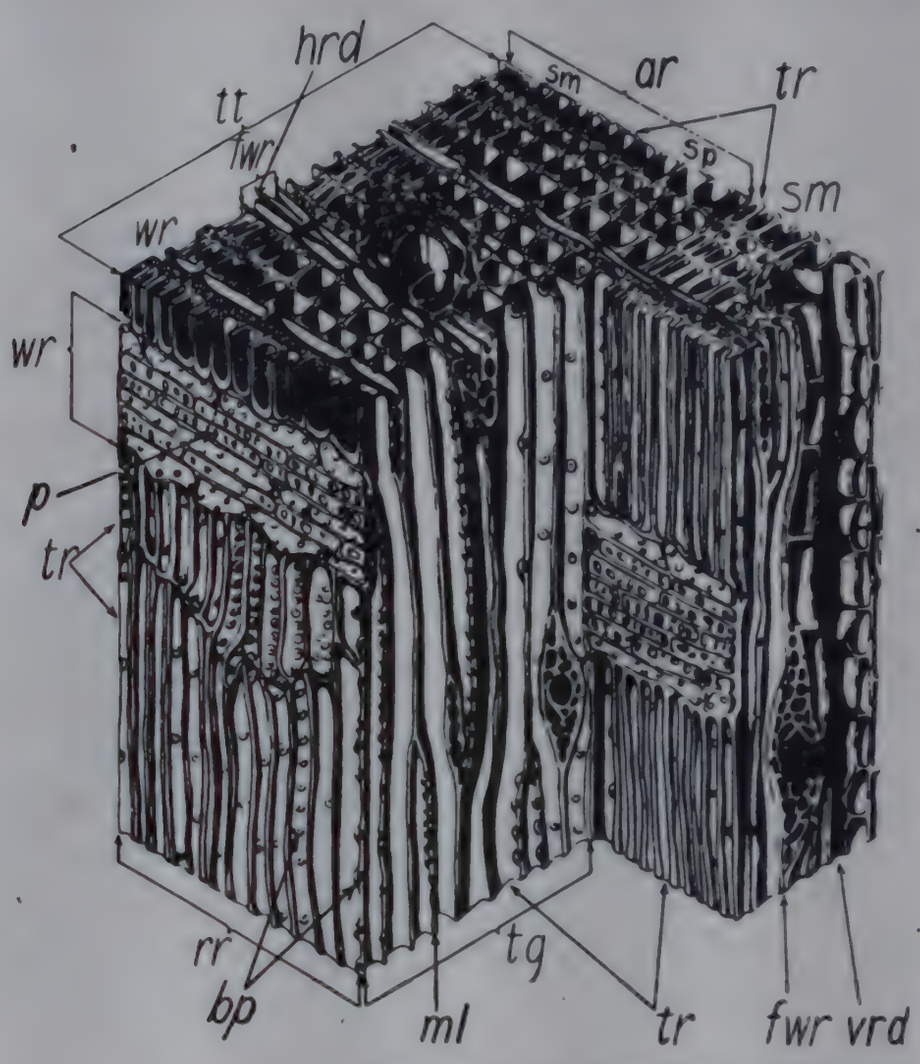
The structural elements of the hardwoods or broad-leaved species differ considerably from those of softwoods or needle-leaved species in morphology and size. These differences are apparent from a study of Figures 29 and 30, which represent small blocks of the two classes of woods.

A transverse section of wood, *tt*, of Figures 29 and 30 shows that the substance is a heterogeneous cellular structure in that it consists of zones known as annual rings, *ar*, each of which represents the radial growth of the tree during one year. The causes for the heterogeneous structure are mainly the variations in the relative size of the cell cavities of the wood. If the ratio of the cell cavity to the cell wall is small, the wood appears dense; if the ratio of the cell cavity to the cell wall is large, the wood appears porous or light.

Both hardwoods and softwoods are composed of cells arranged in two systems. One system is longitudinal, which is parallel to the long central axis of the tree. The other system is radial, which is perpendicular to the long central axis of the tree. The two systems in the hardwoods differ in some respects from those in the softwoods.

Cells of the longitudinal system in the hardwoods consist of wood fibers, *wf*, and vessels, *v*, Figure 29. The fibers that have large cavities develop during the early part of the growing season and form the springwood portion, *sp*, of the annual rings. The fibers that have small cavities develop during the late part of the growing season and form the summerwood portion, *sm*, of the annual rings. Hardwood fibers average about 1 mm. in length and 0.01 mm. in diameter. Vessels consist of short ringlike segments arranged to form tubes which have diameters considerably greater

than those of the fibers. These tubes are connected end to end to form long cylinders which function as longitudinal conductors of liquids in the tree. Vessels in some of the woods such as white oak are filled with inflated balloon-like projections called tyloses. These balloon-like structures



Courtesy of U. S. Forest Products Laboratory

FIG. 30.—DIAGRAM OF BLOCK OF SOFTWOOD.

tt.	Transverse surface.	*ar.*	Annual ring.
rr.	Radial surface.	*wr.*	Wood ray.
tg.	Tangential surface.	*hrd.*	Horizontal resin duct.
tr.	Tracheids.	*p.*	Simple pit.
vrd.	Vertical resin duct.	*bp.*	Bordered pit.
sp.	Springwood.	*fwr.*	Fusiform wood ray.
sm.	Summerwood.	*ml.*	Middle lamella.

Magnification × 90 diam.

are formed by a protrusion of the middle lamella through the pit orifice and into the vessel cavity. They retard impregnation of the wood with wood preservatives in commercial practice.

The radial cellular system of hardwoods consists of wood rays, *wr*, which

are composed of short, slender ray cells arranged with their long axes radially in the tree. They are the conductors of liquids from the bark toward the center of the tree and vice versa, and further act as a storehouse for plant food.

Softwoods have a longitudinal cellular system consisting principally of tracheids, *tr*, and resin ducts, *vrd*, in Figure 30. The tracheids average approximately 3 mm. in length and 0.03 mm. in diameter. Tracheids that develop during the early growing season have large cell cavities and form the springwood, *sp*, whereas those that develop in late growing season have small cell cavities and form the summerwood, *sm*. Tracheids of the softwoods are arranged in better radial alignment than the fibers in the hardwoods. Their cross-sectional area has an approximate rectangular shape, whereas that of the hardwood fibers more nearly approaches a pentagonal or circular shape. Vertical resin ducts, *vrd*, also form a part of the longitudinal cell system of softwoods. They are much larger in diameter than the tracheids. As their name indicates, they form storage space for wood resins.

The horizontal cell system of the softwoods consists of wood rays, *wr*, Figure 30, which are composed of short blunt ray cells and, in some cases, also of horizontal resin ducts, *hrd*. Wood rays having horizontal resin ducts are broad in the tangential direction of their cross section and are known as fusiform wood rays, *fwr*, on account of the shape of the r cross section.

The two cellular systems of both the hardwoods and the softwoods are held together by an intercellular cementing material known as the middle lamella, *ml*, Figures 29 and 30.

Communication between the various fibers, vessels, tracheids, ray cells, etc., takes place through pits extending through the cell walls and through tiny pores in the middle lamella.

The radial walls of the tracheids and the ray cells of the softwoods are profusely perforated by simple pits, *p*, and bordered pits, *bp*, in Figure 30. A similar condition exists in the radial walls of the fibers and the ray cells of the hardwoods except that the pits are mostly of the simple type and smaller than those in the softwoods. Only a few of the pits normally present are indicated by means of dots on the radial walls of the ray cells and vessels and also as circles, *k*, on the walls of the vessels.

The fibers of the hardwoods and the tracheids of the softwoods make up most of the pulp produced by commercial pulping processes. These two structural elements of wood apparently contain a higher percentage of cellulose than do the ray cells. They, accordingly, remain intact in the

bleached pulp and are retained on the screens. Ray cells are much smaller than the fibers and the tracheids, and the smaller ones are accordingly lost during the mechanical handling of the pulp. Further, they contain high percentages of readily soluble hemicelluloses, which dissolve during the pulping process and thereby allow their more stable residual cellulose structure to disintegrate into fragments too small to be retained on the pulp screens.

Other cellular structures such as parenchyma cells, fiber tracheids, and the parts of the various types of pits found in wood are beyond the scope of this condensed topic on wood structure in a chapter on the structure and properties of cellulose fibers.

The steaming and the bending of wood referred to previously are utilized extensively in the furniture and cooperage industries. Steam applied to wood at 160 to 180°C. softens the ligneous and hemicellulosic materials and allows the cellular elements to slip over one another under flexion. If cooled under this condition, the wood sets in the distorted condition, as demonstrated by chair backs and barrel staves.

Several types of materials such as aniline and formaldehyde plasticize wood. If it is impregnated with these materials and subsequently subjected to heat and pressure, it can be molded into variously shaped articles of commerce.

As previously stated, commercial wood pulps are composed largely of the tracheids of softwoods or the fibers of hardwood, depending on the species of wood employed. On account of their thin walls and large cavities, the springwood tracheids and fibers of chemically prepared commercial pulp collapse in the form of ribbons. The thick-walled summerwood tracheids and fibers, on the other hand, remain inflated. Collapsed springwood fibers impart flexibility to paper, whereas inflated summerwood fibers impart stiffness to the paper. Thus, pulps made from wood having high percentages of summerwood produce a stiffer, more open paper than those made from wood having low percentages of summerwood.

Since softwood pulps are composed of longer fibrous elements than hardwood pulps, they produce stronger paper than the latter because of the larger fiber-fiber bonding surface. They are also more easily mechanically handled and processed without loss than are those from hardwood in the manufacture of high alpha pulps and cellulose derivatives. This subject will be fully discussed in Chapter VII.

C. MICROSCOPIC INVESTIGATION

CHARLES W. HOCK, H. MARK, AND GEORGE R. SEARS

1. Investigation with Visible Light*

Cellulose is found almost exclusively in plant tissues, where it comprises the principal constituent of the cell walls. These walls exhibit diverse structural patterns depending upon the orientation of the cellulose and other constituents of which they are composed. Nevertheless, in spite of these differences in microscopic appearance, cellulosic materials from various sources show certain general structural similarities which appear to be fundamental. Some of the more important of these materials are discussed in the following sections.

(a) *Microscopy of Native Sources of Cellulose*

Seed Hairs. Seed hairs are so named because they arise as cellular outgrowths of the seed coat. Of all these hairs which are used commercially, the cotton fiber is unquestionably the most important. Because of its great economic value the attention of many investigators has been directed toward a study of this fiber, and consequently considerable information concerning its structure and behavior is available.

The wall of the cotton fiber is composed of a primary and a secondary part. The former is the outer sheath of the fiber, or the portion of the wall laid down as the fiber increases in length. Secondary wall refers to that part of the wall which is formed after the fibers cease to elongate appreciably. Only the thin primary wall (cuticle) is present as the cotton fiber elongates during the first 15 to 20 days of its growth. Thereafter the thickness of the wall is increased by a deposition of cellulose which comprises the secondary wall. The latter is laid down on the inside of the primary wall, thereby decreasing the size of the central canal or lumen.

The primary wall is exceedingly thin, being only 0.5 μ or less in thickness. Under ordinary conditions of microscopic observation it shows no evidence of internal structure. However, when the wall is stained with a dye such as Congo red and then examined with a polarizing microscope the

* Contributed by Charles W. Hock and H. Mark.

cellulose is found to be present as criss-crossing strands which give a net like appearance to the wall [1–4] (Fig. 31). Cellulose is not, however, the only constituent of the primary wall. The latter also contains wax and pectic materials which may be detected by applying various stains to the fiber, as well as by direct chemical analysis. When young fibers are extracted in

FIG. 31.—CELLULOSE IN THE PRIMARY WALL.

An immature cotton fiber stained with Congo red and photographed between crossed nicols to show the netlike structure of the cellulose in the primary wall.

Magnification × 900.

solvents and cooked in alkali with a minimum of mechanical agitation, the wax and pectin may be removed, leaving only the delicate framework of cellulose. The latter reacts positively to microchemical color tests for cellulose and is soluble in cuprammonium hydroxide reagent. It appears, therefore, that the primary wall is made up of a tenuous network of cellu-

[1] W. L. Balls, *Proc. Roy. Soc. (London)*, **B72**, 72 (1923).

[2] W. L. Balls, *Studies of Quality in Cotton*. Macmillan, London, 1928.

[3] D. B. Anderson and T. Kerr, *Ind. Eng. Chem.*, **30**, 48 (1938).

[4] C. W. Hock, R. C. Ramsay, and M. Harris, *J. Research Natl. Bur. Standards*, **26**, 93 (1941); *Am. Dyestuff Reptr.*, **30**, 53 (1941); *Textile Research*, **11**, 200 (1941).

lose strands intimately associated with a membrane of wax and pectic substance. Although it comprises only a relatively small part of a mature cotton fiber, the primary wall may greatly influence surface properties which play a prominent role in dyeing, finishing, and other processing of cotton.[5, 6]

The principal chemical constituent of cotton, and the one chiefly responsible for its usefulness to man, is cellulose. Although the coarser de-

FIG. 32.—LAMELLAE IN THE SECONDARY WALL.

Cross section of a mature cotton fiber swollen in cuprammonium hydroxide to show lamellae. Stained with Congo red.
Magnification × 400.

tails of structure of the secondary wall are often visible in unswollen material, the pattern is studied to better advantage in expanded sections. While it is recognized that treatment with swelling reagents produces some distortion, this technique appears justifiable, especially since one obtains corroborative evidence from polarization studies and x-ray examinations.

Swollen cross sections of cotton fibers clearly reveal a layered pattern (Fig. 32). Alternating layers stain deeply and lightly with cellulose dyes,

[5] R. Haller, *Z. Farben-Ind.*, **6**, 125 (1907).

[6] A. M. Sookne and M. Harris, *J. Research Natl. Bur. Standards*, **26**, 65 (1941); *Am. Dyestuff Reptr.*, **30**, 29 (1941); *Textile Research*, **11**, 307 (1941).

and between crossed nicols appear either strongly or weakly birefringent The layered structure of the secondary wall can also be seen in longitudina view, where stripes running parallel to the fiber axis and extending from th lumen to the primary wall are observable. Investigation of the formatio of these layers indicates that two adjacent layers, one compact and on porous, are deposited every 24 hours, and together constitute a daily "growth ring."[4, 7, 8] Counts of rings in fibers of different ages show that on

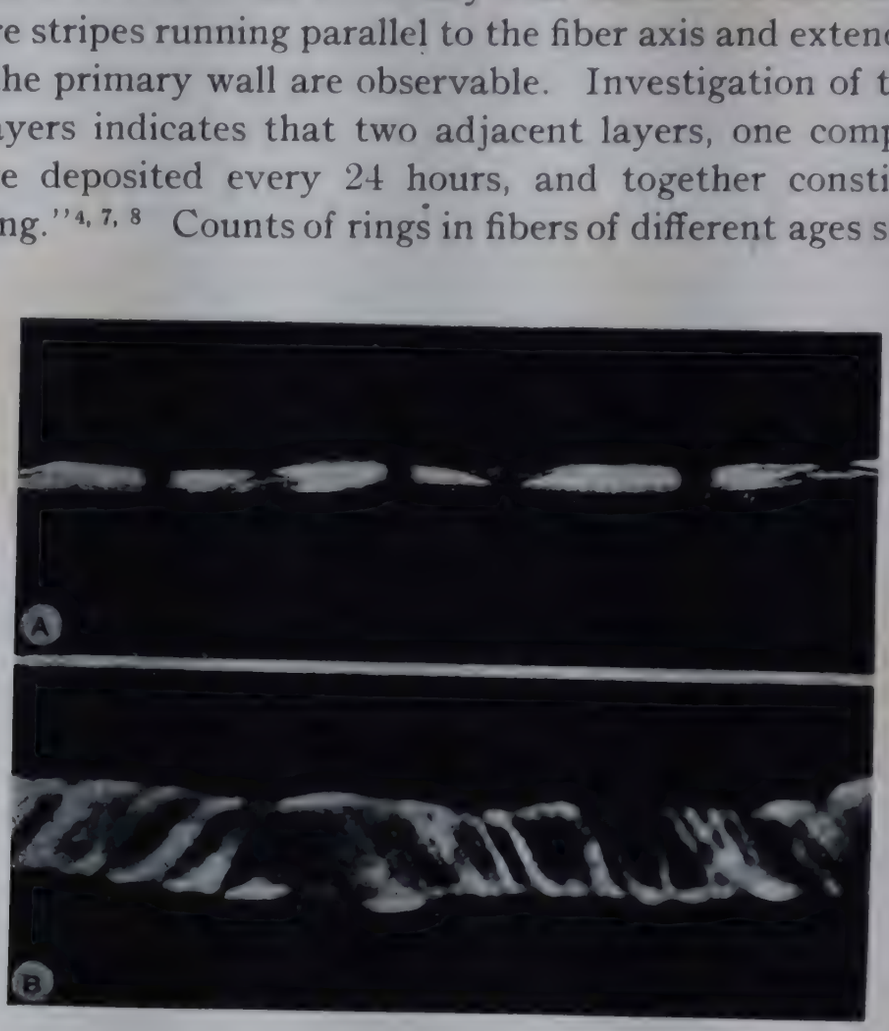


FIG. 33.—DIFFERENCES IN ORIENTATION OF THE FIBRILS.

A. An unswollen mature fiber photographed between crossed nicols to show the bands of extinction.

Magnification × 130.

B. Slightly swollen fiber showing a reversal in direction of winding of the fibrils.

Magnification × 310.

ring is laid down per day until the fiber reaches maturity. The width of individual growth rings varies from 0.1 to 0.5 micron, and appears to fluctuate with variations in environmental conditions.

Upon examination of single cotton fibers with the crossed nicols of a polarizing microscope, much can be learned about the orientation of the cellulose. When placed approximately parallel to the plane of light passing through one of the nicol prisms, the high birefringence of the fibers is interrupted by bands of extinction which are randomly placed in re-

[7] W. L. Balls, *Proc. Roy. Soc.* (*London*), **B90**, 342 (1919).

[8] T. Kerr, *Protoplasma*, **27**, 229 (1937).

spect to the natural convolutions or twists of the fiber (Fig. 33A). These optical variations can be correlated with differences in structure observed in slightly swollen fibers. Upon swelling, the fiber is found to consist of innumerable fine spirally-wound fibrils which make either an S or Z twist,[9]

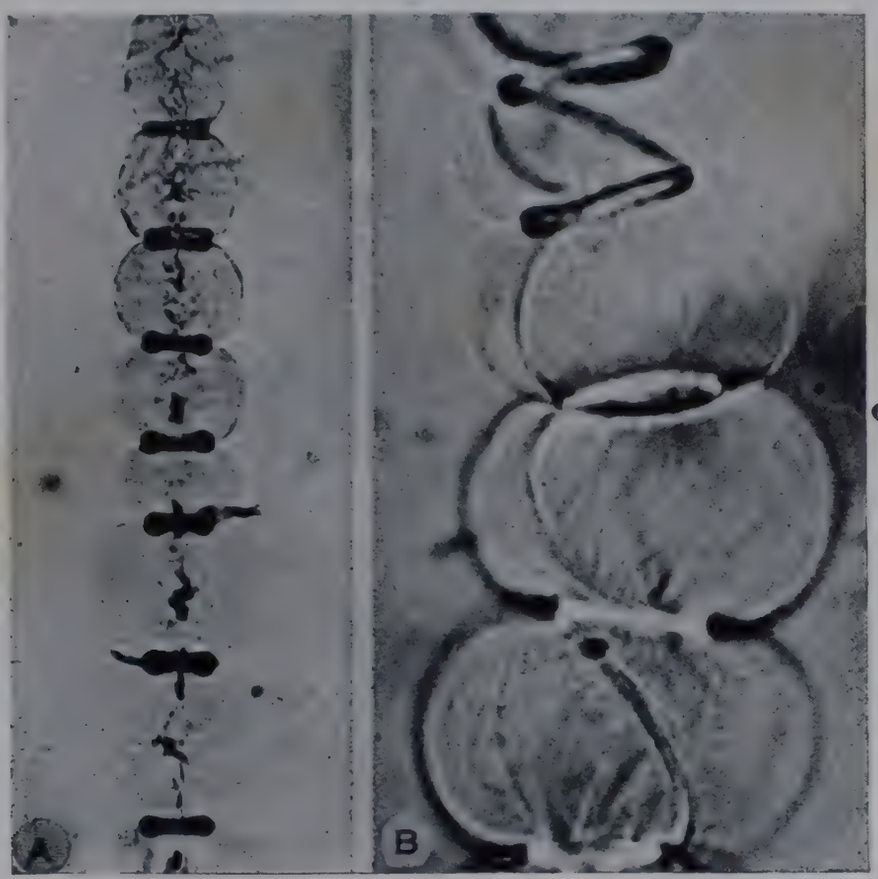


FIG. 34.—SWELLING OF COTTON FIBERS IN CUPRAMMONIUM HYDROXIDE.

A. A raw cotton fiber.

Magnification × 100.

B. A purified fiber in which the wax and pectic substance had been removed by previous chemical treatments.

Magnification × 500.

reversal of direction taking place many times in a single fiber (Fig. 33B). It can be shown, moreover, that the bands of extinction observed between crossed nicols actually are the places where the fibrils reverse their direction of twist. In certain types of cotton, at least, the direction of winding of the

[9] According to *A.S.T.M. Standards on Textile Materials*,[10] a yarn or cord has an S twist if, when held in a vertical position, the spiral conforms in slope to the central portion of the letter S, and a Z twist if the spiral conforms to the central portion of the letter Z. In the present paper the same terminology will be applied to fibrils.

[10] *A.S.T.M. Standards on Textile Materials.* Am. Soc. for Testing Materials. Philadelphia, 1941.

fibrils in the first-formed layer of the secondary wall is opposite from tha in the layers which are laid down subsequently. In other words, if th outermost layer of fibrils makes an S twist, the fibrils in the remainin layers made a Z twist. Since the fibrils in all the layers reverse thei direction at the same place this constant relationship is maintained.

When mature cotton fibers are placed in certain reagents, the cellulose o the secondary wall expands rapidly and often causes the primary wall t rupture. As the cellulose continues to push through these breaks, ex panded regions resembling beads appear along the axis of the fibe (Fig. 34A). This type of swelling is characteristic of raw mature cotton fibers. It has long been recognized that the primary wall is responsible, a least in part, for this uneven swelling.[3, 4, 11–16] The rupture of this wall into a series of constrictions which restrain the expanding cellulose has frequently been described and photographed. It is interesting to note, however, tha after certain treatments, similar swelling occurs in fibers which have had the primary wall removed by previous chemical procedures.[17] In such cases, the outermost layer of fibrils in the secondary wall becomes clumped and prevents uniform lateral expansion (Fig. 34B). Thus, it appears that irregular swelling along the fiber axis depends in part on the orientation of the cellulose fibrils as well as on the primary wall.[4] In raw fibers the swelling cellulose may push through the outer layer of fibrils and also the primary wall, so that a constriction in such cases consists of clumped fibrils as well as of a portion of the primary wall.

Other seed hairs which have a minor commercial use include bombax cotton (*Bombax sp.*), true kapok (*Eriodendron anfractuosum*), and hairs of the common milkweed (*Asclepias sp.*).

Bast Fibers. Morphologically, the fibers of stems may be classified as wood and bast fibers. The latter include fibers from the cortex, the pericycle, and the phloem, and differ anatomically from those of the xylem or wood.

The principal bast fibers of commerce are flax, hemp, ramie, and jute. They vary considerably in length, ranging from a few inches to over a foot. Each of these fibers is composed of smaller elements or cells. Whereas the

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[11] E. Schweizer, *J. prakt. Chem.*, **72**, 109 (1857).
[12] C. Cramer, *J. prakt. Chem.*, **73**, 1 (1858).
[13] H. J. Denham, *J. Textile Inst.*, **14**, T86 (1923).
[14] T. B. Bright, *J. Textile Inst.*, **17**, T396 (1926).
[15] G. G. Osborne, *Textile Research*, **5**, 275 (1935).
[16] W. K. Farr, *Contrib. Boyce Thompson Inst.*, **10**, 71 (1938).
[17] R. K Worner and R. T. Mease, *J. Research Natl. Bur. Standards*, **21**, 609 (1938).

cotton fiber is a single plant cell, the bast fiber as used industrially is made up of a number of individual cells, which together produce a fiber of high tensile strength. Flax, hemp, and jute fibers are separated from the woody part of the stem by a process known as retting. The separation of ramie fibers appears to be a difficult process and is usually carried out by hand. This has been the chief reason for the limited use of this fiber.

In cross section, commercial flax fibers are seen to consist of several polygonal cells with straight smooth sides, which probably account for some

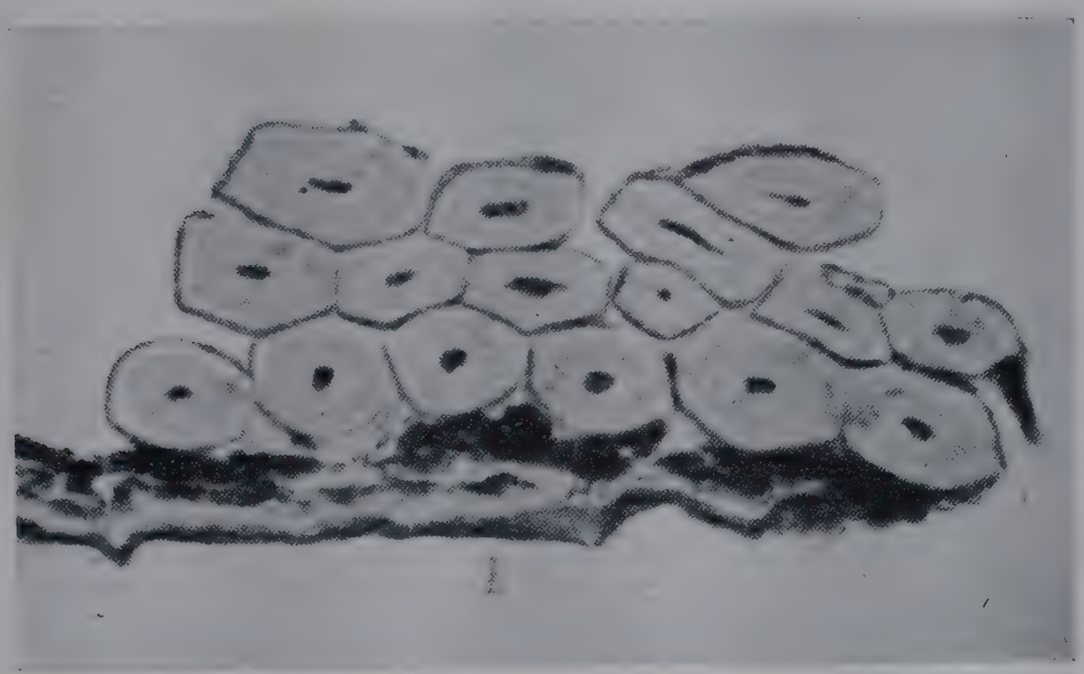


FIG. 35.—CROSS SECTION OF A FLAX FIBER (HERZOG[18]).

Part of the "bark" remains attached to a group of flax cells. Stained with iodine and sulfuric acid.

Magnification × 330.

of the luster associated with linen (Fig. 35). The walls of the cells are very thick so that the lumen is reduced to a fine canal. Upon staining with ruthenium red,[19] the outer margins and the region around the lumen take on a deep red color. When flax fibers are treated with cuprammonium hydroxide, iodine and sulfuric acid, and certain other reagents,[20, 21] the fibers swell greatly in diameter and the layered structure of the wall becomes in-

[18] A. Herzog, *Die Unterscheidung der Flachs und Hanffaser.* J. Springer, Berlin, 1926.

[19] Although ruthenium red is not a specific stain for pectic substance, native pectic compounds usually take a red color in the presence of this dye.[3]

[20] C. R. Nodder, *J. Textile Inst.*, **13,** T161, T213 (1922).

[21] D. B. Anderson, *Am. J. Botany*, **14,** 187 (1927).

creasingly prominent. The number of these layers varies, as many as fifty having been counted in some cells. As in the cotton fiber, alternating layers differ in their ability to take up dyes and also appear unlike between crossed nicols. There is a greater number of these layers in the walls of the flax cells at the base of the stem than in the cells from the growing tip.

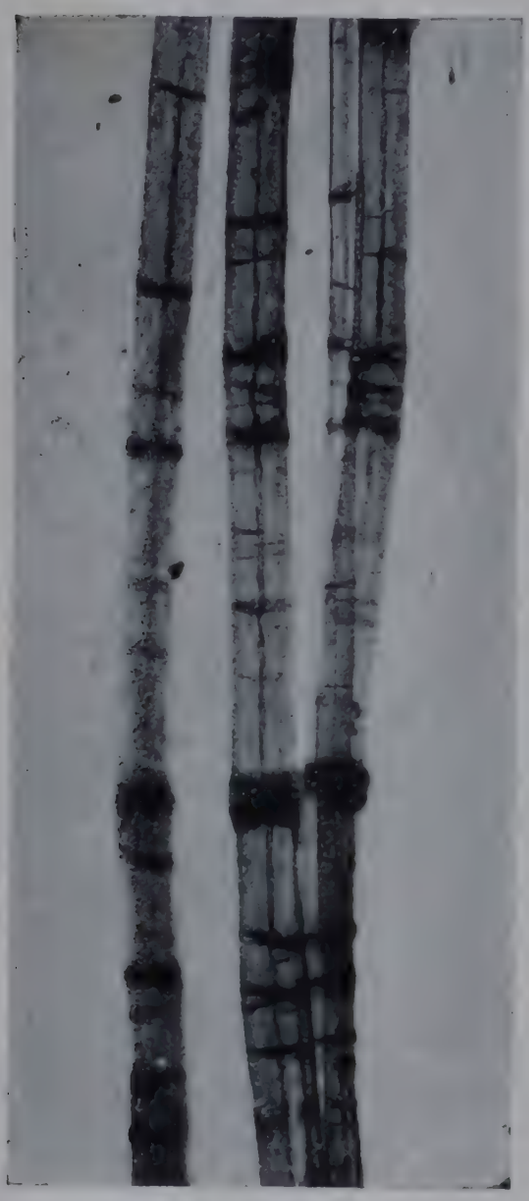


FIG. 36.—'DISLOCATIONS" IN FLAX CELLS.

Stained with zinc chloride-iodine.

Magnification × 200.

Entire flax cells can be separated from the bundles by treatment with caustic soda, which dissolves all or part of the pectic materials which bind the cells together. These cells vary from 12 to 25 microns in diameter and from a few hundredths to more than an inch in length.[22, 23] They are pointed, have uniformly thick walls, and a narrow lumen which in longitudinal view appears as a mere line. A characteristic of the cells is the occurrence of "dislocations" on their surfaces. These markings extend transversely and often form the letter "X." They are more apparent after treatment of the fibers with zinc chloride-iodine, whereupon they become darker (Fig. 36). In cuprammonium hydroxide solution the fibers swell, the first signs of attack appearing at the "dislocations." When the flax fibers are swollen in suitable reagents, the walls of the cells are found to be made up of innumerable fine fibrils which give to the swollen cell a distinctly fibrous appearance. These fine filaments or fibrils lie just above the limit of microscopic visibility and are variously grouped and arranged to give the characteristic pattern of the cell wall.

The individual cells of hemp, jute, and ramie show many similarities to those of flax. Although each of these fibers possesses certain proper-

[22] T. F. Hanausek, *The Microscopy of Technical Products*. John Wiley, New York, 1907.

[23] J. M. Matthews, *The Textile Fibers*. John Wiley, New York, 1924.

ties which adapt it for special uses, nevertheless all are sufficiently similar to make identification difficult by microscopic technique.[24]

Wood Fibers. The different types of wood may be placed in two general groups. Coniferous woods, which are obtained from conifers or needle-leaved trees, are commonly referred to as softwoods and include such familiar types as spruce, pine, hemlock, and fir. The second group, or hardwoods, comprises the wood of dicotyledons, which are the broad-leaved deciduous trees such as oak, beech, maple, chestnut, and hickory. For practical as well as for scientific reasons it is convenient to separate these two groups as they have different commercial uses and show distinguishing anatomical characteristics. Fibers from diverse sources differ

TABLE 1

DIMENSIONS OF WOOD FIBERS (HÄGGLUND[25])

Kind of Wood	Length in mm.		Width in mm.	
	Max.	Min.	Max.	Min.
Coniferous woods				
Fir	3.8	2.6	0.069	0.025
Pine	4.4	2.6	0.075	0.030
White spruce	4.2	2.3	...	...
Hemlock	5.0	2.8	...	...
Deciduous woods				
Aspen	1.7	0.8	0.046	0.020
Birch	1.6	0.8	0.040	0.014
Poplar	1.6	0.7	0.044	0.020

from one another, not only in size, but also in respect to shape and other microscopic characteristics.[26] In a single sample of woody material, several types of cellulose fibers of various shapes and markings are present. These types differ, depending on the functions which they perform in the plant, and on the season during which they develop. It is found, for example, that the fibers with thin walls and large central canals develop during the early growing season when moisture in the soil is plentiful, whereas thick-walled fibers with narrow central canals develop during the latter part of the growing season when soil moisture is less abundant. The dimensional properties of several wood fibers are given in the accompanying table from Hägglund[25] (Table 1).

[24] T. M. Plitt, U. S. Dept. of Commerce, *Circ.* **C423** (1939).

[25] E. Hägglund, *Holzchemie.* Akademische Verlagsgesellschaft m. b. H., Leipzig, 1939.

[26] A. J. Eames and L. H. McDaniels, *Introduction to Plant Anatomy.* McGraw-Hill, New York, 1925.

The wood of conifers is relatively simple and homogeneous, consisting of only a few cell types.[26] In a number of cases the wood or xylem is made up principally of tracheids. These are elongated single cells with more or less pointed ends, and thick lignified walls which usually have markings called bordered pits. The lumen or central canal is large and free of contents. The tracheid is, thus, a long, empty, firm-walled tube extending parallel to the long axis of the tree trunk (Fig. 37).

Courtesy of Paper Section, Natl. Bur. Standards

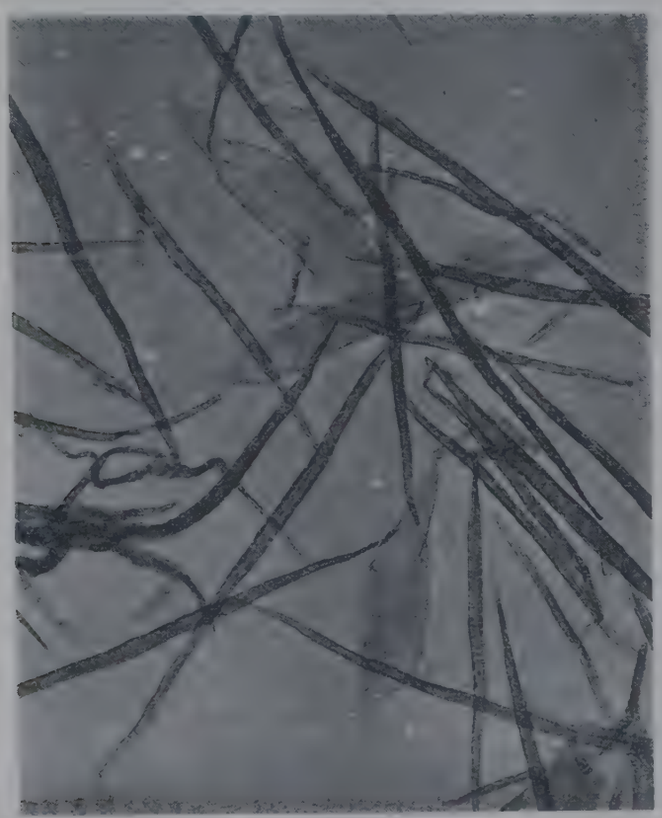
FIG. 37.—INDIVIDUAL CELLS FROM A SOFTWOOD.
Magnification × 50.

Hardwoods, generally, are characterized by a complexity of structure far greater than that of softwoods. This complexity is due to the presence of several kinds of cells (tracheids, vessels, fibers, wood parenchyma cells, and others) and to their arrangement with one another.

Vessels are characteristic of nearly all hardwoods. These are of considerable diameter and length, and arise from the transformation of a row of cells into one tube. The thickening material in the walls is laid down in various patterns, which may be described as annular, spiral, reticulate, or pitted. Unlike the vessels, which are adapted to water conduction, other cells present in the wood are primarily mechanical elements which give the

wood strength and rigidity. These cells are elongated, thickened, and pointed at the ends. Such fibers may reach a length of several inches, and have walls so thick that the lumen is greatly reduced. Between the heavily thickened fibers and the thinner-walled conducting elements all intergrading forms occur (Fig. 38).

Under high magnification the walls of fibers exhibit diverse structural patterns.[27, 28] In cross section these patterns range from concentric to



Courtesy of Paper Section, Natl. Bur. Standards

FIG. 38.—INDIVIDUAL CELLS FROM A HARDWOOD.
Magnification × 50.

radial, or various complex combinations of these simpler types. In some fibers the patterns are readily visible, even in unswollen sections, but in others the sections must first be expanded by the use of suitable swelling reagents before the finer details of structure can be studied. Under these conditions it can be seen that the layers and other coarser structures are further subdivided into a system of fine fibrils which usually lie just above the limit of microscopic visibility. There is evidence, also, that the stria-

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[27] I. W. Bailey, *Ind. Eng. Chem.*, **30,** 40 (1938).

[28] I. W. Bailey, *The Walls of Plant Cells* in *The Cell and Protoplasm*. Science Press, Lancaster, 1940.

tions, which are frequently detectable in the intact wall, are related to the fibrils observed in the swollen material. Although a variety of physical and chemical treatments reveal the presence of fibrils in the cell wall, probably no method gives a more convincing demonstration of their presence than microdissection. Upon handling fibers with microneedles the fine fibrils which comprise the wall can be separated from one another.[29, 30] Where these fibrils are oriented approximately parallel to the long axis of a cell, when observed in swollen cross sections they appear as little specks or granulations. These also may be variously grouped together to give a concentric, radial, or any other pattern which is typical of a particular fiber. In most cases the fibrils do not lie perfectly parallel to the axis of the fiber but are inclined at an angle which may vary in different fibers and even in different layers of a single fiber. It has been shown, moreover, that fibrils in different layers may spiral in opposite directions, thereby giving rise to the so-called crossed fibrillar appearance.

In heavily lignified fibers it is possible to remove the cellulose and leave a firmly coherent residue of lignin; conversely, it is possible to remove the lignin and leave the cellulose matrix.[27, 28] Following Frey-Wyssling's[31] conception of the submicroscopic structure of cellulose (recently supported by additional evidence from studies involving use of the electron microscope, which is discussed later on in this section (p. 316)), a similar configuration has been suggested[32] for the finer visible structure of the cell wall. According to this viewpoint the secondary wall consists of a matrix of cellulose fibrils interpenetrated by a system of interconnecting capillaries which commonly contain pectic substances, hemicelluloses, lignin, and other organic compounds. The differences in the visible patterns of the walls of different types of wood may, therefore, be caused by variations in the orientation of the cellulose fibrils and also by variations in the amount and arrangement of organic substances which are deposited between the fibrils.

Other Cell Walls. Besides the industrially important types of cellulose fibers already described, there are other plant cell walls which, although having no particular commercial value, are of considerable scientific interest. To this class belong the cells of *Valonia* and *Halicystis*. These green algae are characterized by large bubble-like cells, which in some species may be 2 or 3 cm. in diameter. Each cell has a large central vacuole filled with liquid. The vacuole is surrounded by a thin lining of protoplasm,

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[29] W. Seifriz and C. W. Hock, *Paper Trade J.*, **102**, 36 (May 7, 1936).

[30] C. W. Hock and W. Seifriz, *Paper Trade J.*, **110**, 31 (Feb. 1, 1940).

[31] A. Frey-Wyssling, *Protoplasma*, **25**, 261; **26**, 45 (1936); **27**, 372, 563 (1937).

[32] I. W. Bailey, *Bull. Torrey Botan. Club*, **66**, 20 (1939).

which in turn is enclosed by a comparatively thick wall consisting chiefly of cellulose. Because of the large size of the cells it is possible to make observations which limitations of technique make impossible with the small cells of the higher plants.

The wall structure of the cells of *Valonia* has been found to be strikingly similar to that of fibers from other plants.[33, 34] The wall is laid down in microscopically visible layers which may number as high as thirty or forty. Each layer is made up of fibrils whose direction of orientation corresponds to the direction of orientation of the cellulose chains as determined by x-ray methods. It appears that the cellulose fibrils in adjacent layers make an angle of about 80° with each other. In other words, the odd layers have striations or fibrils in one direction, whereas the even layers have fibrils in the opposite direction. The whole wall is, thus, composed of a series of superimposed layers each with its own cellulose chain direction. The results of studies of the walls of these algae give further support to the view that visible striations on the walls of cells are not merely artifacts but correspond closely to the structure of the wall. The above results with *Valonia* have recently been extended to *Cladophora*, which is another closely related green alga but of the filamentous type.[35]

(*b*) *Microscopy of Cellulose in Different Reagents*

In the foregoing discussion special attention was given to manipulative techniques and the use of reagents which reveal the details of structure of the fibers. Two reagents, cuprammonium hydroxide and sodium hydroxide, are used so widely in a number of industrial processes that their effects on the fiber are given additional consideration below.

Cuprammonium Hydroxide Solution. Cuprammonium hydroxide is used not only as a solvent in preparing regenerated fibers but also as a means for dispersing cellulose in order to study certain of its physical and chemical properties. The viscosity of cuprammonium hydroxide solutions has, for example, frequently been related to the quality of cotton, especially as regards its tensile strength and reducing power.[36, 37, 38] It has been shown that chemical treatments which modify the properties of the fibers in such

[33] W. T. Astbury, T. C. Marwick, and J. D. Bernal, *Proc. Roy. Soc.* (*London*) **B109,** 443 (1932).

[34] R. D. Preston and W. T. Astbury, *Proc. Roy. Soc.* (*London*), **B122,** 76 (1937).

[35] W. T. Astbury and R. D. Preston, *Proc. Roy. Soc.* (*London*), **B129,** 54 (1940).

[36] D. A. Clibbens and B. P. Ridge, *J. Textile Inst.*, **19,** T394 (1928).

[37] A. J. Stamm, U. S. Dept. of Agr., *Misc. Pub.* **240** (1936).

[38] G. F. Davidson, *J. Textile Inst.*, **31,** T81 (1940).

a way as to impair their tensile strength also bring about a lowering of the viscosity in cuprammonium hydroxide solutions.[39, 40] On the basis of the molecular chain theory for the structure of cellulose, this decrease in tensile strength, and the accompanying increase in cuprammonium hydroxide fluidity, may be regarded as having resulted from a shortening in average chain length of the cellulose molecules. This point of view is generally held by cellulose chemists and is supported by considerable experimental evidence.

Another point of view, however, was held by Farr and her collaborators. These investigators,[16, 41–44] whose work greatly stimulated research on the structure of cellulose, claimed that the cellulose component of cotton fibers and other cellulosic membranes did not dissolve in cuprammonium solution but maintained a visible state of aggregation in the form of small cellulose particles, each of which was surrounded by cementing material which swelled in cuprammonium solution and thereby gave rise to a gel-like structure upon which characteristic properties of the dispersion depended. On the basis of this interpretation it followed that the reduction of viscosity through processing or deterioration of the fibers was to be regarded as the result of a direct effect upon the viscosity-producing power of the cementing material.

The viewpoint of Farr was based principally on microscopic observations. To the particles which persisted in cuprammonium hydroxide, dimensions[16] of 1.5 × 1.1 μ, and an apparent density[45] of 1.5 were attributed. The cementing material which was said to bind the somewhat ellipsoidal particles together to form fibrils, and the fibrils together to form lamellae, was stated to consist, at least in part, of pectic compounds,[16, 41] although at other times the pectic nature of this material was doubted,[46] and only recently it was stated that "the chemical composition of this colloidal substance is complex and not adequately analyzed."[47] Nevertheless, a consideration of pectin[16] and pectic substances has figured largely in the experiments of the supporters of the particle hypothesis. The existence of

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[39] R. T. Mease and L. F. Gleysteen, *J. Research Natl. Bur. Standards*, **27**, 543 (1941).

[40] R. L. Whistler, A. R. Martin, and M. Harris, *J. Research Natl. Bur. Standards*, **24**, 555 (1940); *Am. Dyestuff Reptr.*, **29**, 244 (1940); *Textile Research*, **10**, 269 (1940).

[41] W. K. Farr and S. H. Eckerson, *Contrib. Boyce Thompson Inst.*, **6**, 189 (1934).

[42] W. K. Farr, *J. Phys. Chem.*, **42**, 1113 (1938).

[43] J. Compton, *Contrib. Boyce Thompson Inst.*, **10**, 113 (1938).

[44] W. A. Sisson, *Contrib. Boyce Thompson Inst.*, **10**, 57 (1938).

[45] J. Compton, *Ind. Eng. Chem.*, **31**, 1250 (1939).

[46] W. K. Farr, *J. Phys. Chem.*, **41**, 987 (1937).

[47] H. R. Mauersberger, *Rayon Textile Monthly*, **21**, 413 (1940).

uch a cementing material as a fundamental or essential constituent of the otton fiber is questionable since it has been recently shown that the presnce or absence of pectin has no appreiable influence upon the viscosity of otton in cuprammonium solution or ıpon the strength of the fibers.[40, 48, 49] Thus, the viscosity is an intrinsic property of the cellulosic substance and not of the material which may be extracted from the fiber.

In a recent investigation,[50] cotton fibers which had been purified in various ways were treated with cuprammonium hydroxide solution in an effort to repeat the observations of Farr and her coworkers. It was found, however, that during treatment of cotton with cuprammonium reagent, the cellulose dissolved, leaving residues which varied in amount and in structure depending upon the extent of purification of the fibers. The undissolved residue from raw and from dewaxed fibers (Fig. 39, A and B) consisted of fragmented primary walls, and to a lesser extent of material from the lumen. Both of these residues were isotropic, and upon analysis were found to consist largely of pectic substance.[40, 50] Fibers which were further purified by the removal of both wax and pectic compounds dissolved completely in the reagent. In none of these experiments were cellulose particles observed to persist in the solution. However, under certain conditions of examination, ellipsoidal particles, 1–2 μ in size, did appear in the system (Fig. 40). It was shown that these particles arise in cuprammonium solution whether

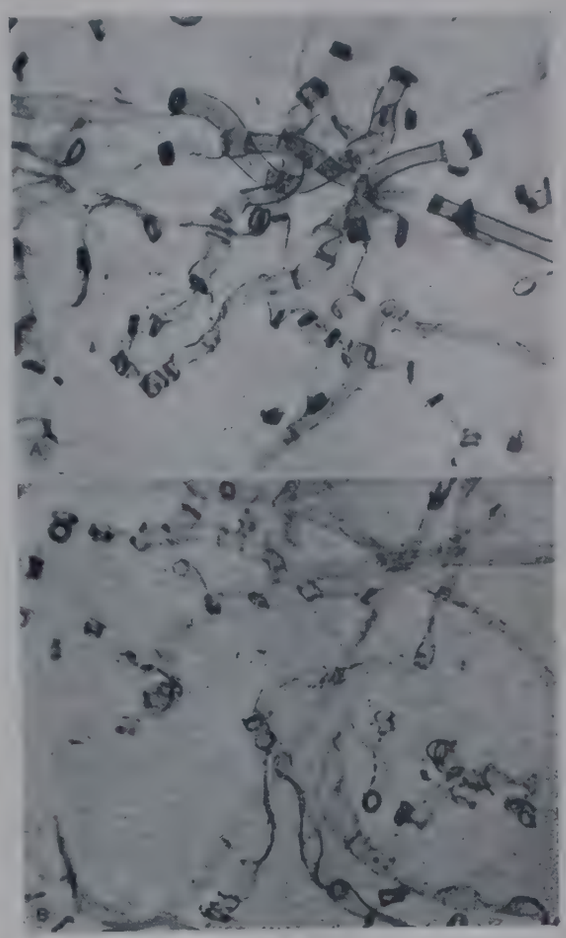

FIG. 39.—RESIDUE WHICH REMAINS AFTER TREATMENT OF COTTON FIBERS WITH CUPRAMMONIUM REAGENT.

A. Residue from raw fiber .
B. Residue from dewaxed fibers.
Fibers stained with ruthenium red. Magnification × 60.

[48] E. Heuser and J. W. Green, *Ind. Eng. Chem.*, **33**, 868 (1941).

[49] H. F. Lewis, F. E. Brauns, and M. A. Buchanan, *Paper Trade J.*, **110**, 36 (Feb. 1, 1940).

[50] C. W. Hock and M. Harris, *J. Research Natl. Bur. Standards*, **24**, 743 (1940); *Am. Dyestuff Reptr.*, **29**, 287 (1940); *Textile Research*, **10**, 323 (1940).

or not cellulose is present, and result from the exposure of the reagent to air. It is concluded from this investigation that microscopically resolvable particles of cellulose do not persist in cuprammonium hydroxide under the experimental conditions applied.

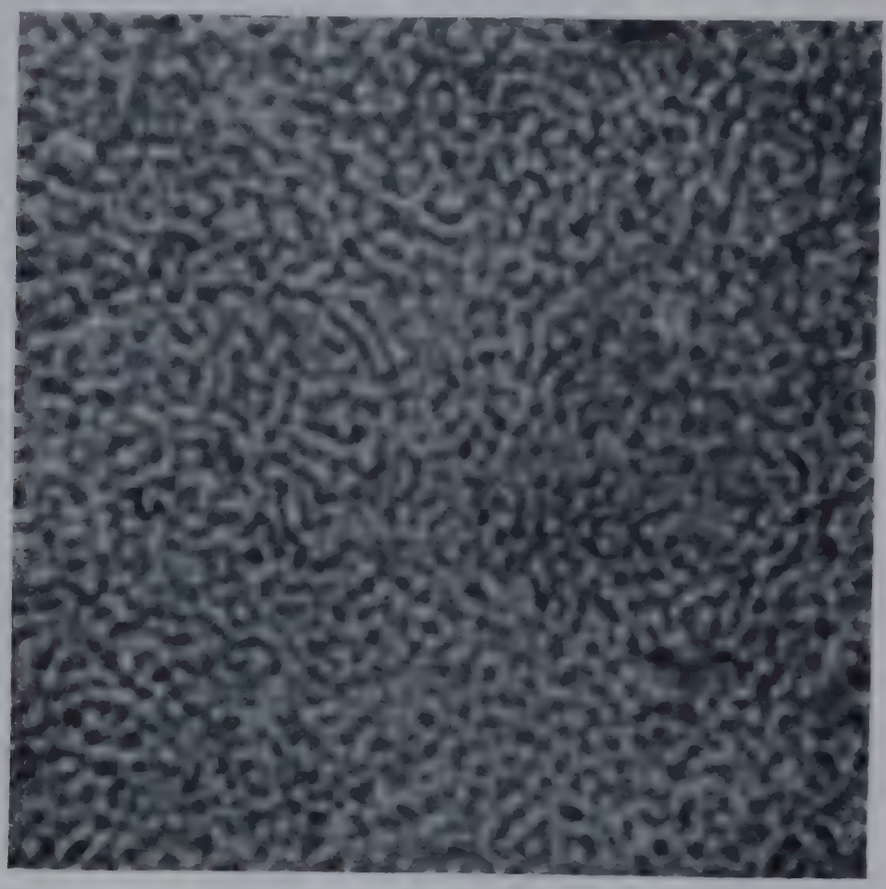

FIG. 40.—PARTICLES IN CUPRAMMONIUM HYDROXIDE. Particles formed upon exposure of the reagent to air. No cellulose present.

Magnification × 1000.

Sodium Hydroxide Solution. When cotton and other plant fibers are treated with sufficiently concentrated alkali, a reaction occurs which is commonly spoken of as mercerization. Fibers which have been treated in this way show an increase in tensile strength, an improved luster, and a greater affinity for certain dyes. A microscopic examination of mercerized fibers shows that they have a different structural appearance from unmercerized cotton.[22, 23]

The cotton fiber is normally flat and ribbon-like with many convolutions or twists. Upon placing it in alkali, swelling takes place and the fiber presents the appearance of a hair rather than a flat ribbon. As swelling proceeds, the filament untwists, becomes much straighter, and at the same time decreases considerably in length (Fig. 41A). In most mercerizing

processes tension is applied to the fibers in order to minimize shrinking, and this produces further microscopic differences. For example, whereas fibers merely treated with alkali still have a somewhat roughened and

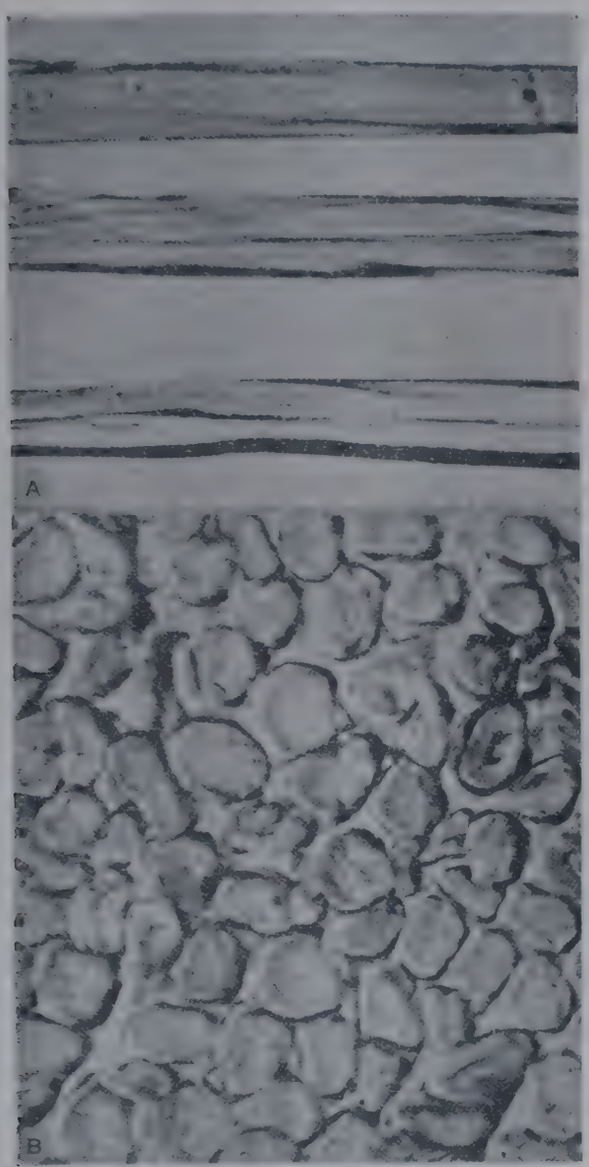

FIG. 41.—MERCERIZED COTTON FIBERS (VON BERGEN AND KRAUSS[51]).

A. Surface view.
B. Cross sections.
Magnification × 75.

wrinkled surface, after stretching they are almost straight and rigid and show a smooth surface which accounts in part for the luster of mercerized fibers. The lumen appears reduced in diameter or may even disappear. Although many of these characteristics may be observed in surface view,

[51] W. von Bergen and W. Krauss, *Rayon Textile Monthly*, **21**, 441 (1940).

they can be studied to better advantage in cross section. Thus, whereas cross sections of ordinary cotton fibers appear as collapsed tubes with irregular kidney shapes, the alkali-treated sections are more or less circular with a small lumen (Fig. 41B). In spite of these differences in microscopic appearance, the identification of mercerized and unmercerized cotton is by no means easy. Part of the difficulty may arise from the fact that all degrees of mercerization may occur in a single sample. Many fibers, especially in yarn, may remain in their original form, whereas others may be mercerized in only portions of their length.

There are a few ways, however, in which one can sometimes distinguish, qualitatively, mercerized from unmercerized samples. One means that is useful depends upon the removal of parts of the primary wall of the fiber by the caustic soda used in mercerization. When fibers treated in this way are placed in cuprammonium hydroxide, "balloons" are not formed as readily since the weakened primary wall or cuticle is not strong enough to prevent uniform expansion of the fiber. Untreated fibers, when given the same treatment, give rise to many more irregular swellings along the fiber axis. Other tests based on the use of dyes, of polarized light, and other aids have been suggested as a means of distinguishing mercerized and unmercerized cotton, but these have not been found satisfactory for general use.[23, 52]

Mercerizing is usually confined principally to cotton. Flax, however, is sometimes treated in this way also and, in general, essentially the same changes in appearance take place. The fiber becomes more rounded, the lumen is further restricted, and the dislocation marks are not so readily observed.[52]

(c) *Microscopy of Rayons*

The physical properties of artificial textile fibers are controllable within rather wide limits by the spinning conditions. Thus, the size of the filaments, the shape of the cross sections, and the character of the surface may vary depending upon the conditions of manufacture, particularly upon the composition of the coagulating bath used and upon the mechanical stretch during spinning. There are, nevertheless, certain microscopic properties which are characteristic of the different classes of artificial fibers.[10, 24, 53]

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[52] P. Heerman and A. Herzog, *Mikroskopische und mechanisch-technische Textiluntersuchungen*. J. Springer, Berlin, 1931.

[53] H. R. Mauersberger and E. W. K. Schwarz, *Rayon and Staple Fiber Handbook*. 3rd ed., Rayon Handbook, New York, 1939.

For certain uses rayons with a dull luster are considered desirable. Since many of these fibers ordinarily possess a high degree of luster it is necessary to treat them so as to bring out the desired property. The reduction of luster is brought about in several ways. It is done chiefly by increasing the roughness of the surface during manufacture or by the impregnation of opaque pigments or precipitates on the surface or within the filaments of the yarn. Where delustering is effected by fiber impregnation, cross sections show the pigments scattered in varying concentrations throughout the fiber. Observations made by dark-field illumination are especially useful in this connection.[54–57]

Viscose. As observed in longitudinal view, the type of viscose rayon commonly found on the market today has a striated or fluted appearance (Fig. 43A). The surface of the fibers can be studied to good advantage by the R-O-X embedding method of Reumuth.[58, 59] This method consists essentially of embedding only the lower half of the fiber in a medium of refractive index corresponding to that of the fiber, so that the lower half is optically eliminated, and the remaining upper half appears to better advantage in the microscope. Using this method, Reumuth and his collaborators[60] have examined and described the surface character of many artificial textile fibers (Fig. 42).

Cross sections are especially useful for the identification of different rayons. Because of their irregular shapes the dimensions of rayons are difficult to define numerically although attempts at this have been made.[61, 62] The shape of the fiber shows up to better advantage in cross section and is often distinctive enough to allow presumptive identification. Viscose fibers are irregular, with a scalloped or serrated contour (Fig. 43B). The investigation of certain defects in viscose, as in other rayons, can be carried out on cross sections. As pointed out by Preston[57] a bad spinneret in which one hole is partly blocked gives rise to a fine weak filament which can be detected readily in cross section. Similarly, fine cracks, other internal flaws, and a sticking together of the fibers can be seen. The skin effect of viscose rayon can be observed when cross sections are swollen.

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[54] N. Gaidukov, *Z. angew. Chem.*, **21**, 393 (1908).
[55] J. Schneider and G. Kunzl, *Z. wiss. Mikroskop.*, **23**, 393 (1906).
[56] A. Herzog, *Textile-Forsch.*, **3**, 1 (1921).
[57] R. D. Preston, *Modern Textile Microscopy*. Emmott, London, 1933.
[58] H. Reumuth, *Klepzig's Textil-Z.* **39**, 612 (1936).
[59] H. Reumuth, W. Kling, and H. Schwerdtner, *Kunstseide*, **19**, 247 (1937)
[60] H. Reumuth, *Kunstseide*, **21**, 286 (1939).
[61] A. Herzog, *Textile-Forsch.*, **3**, 99 (1922).
[62] H. Schloemer, *Kunstseide*, **12**, 380 (1930).

stained, or examined between crossed nicols. Under these conditions the surface layer shows differences from the interior of the fiber. The skin always appears to have at least planar orientation of the crystallites,

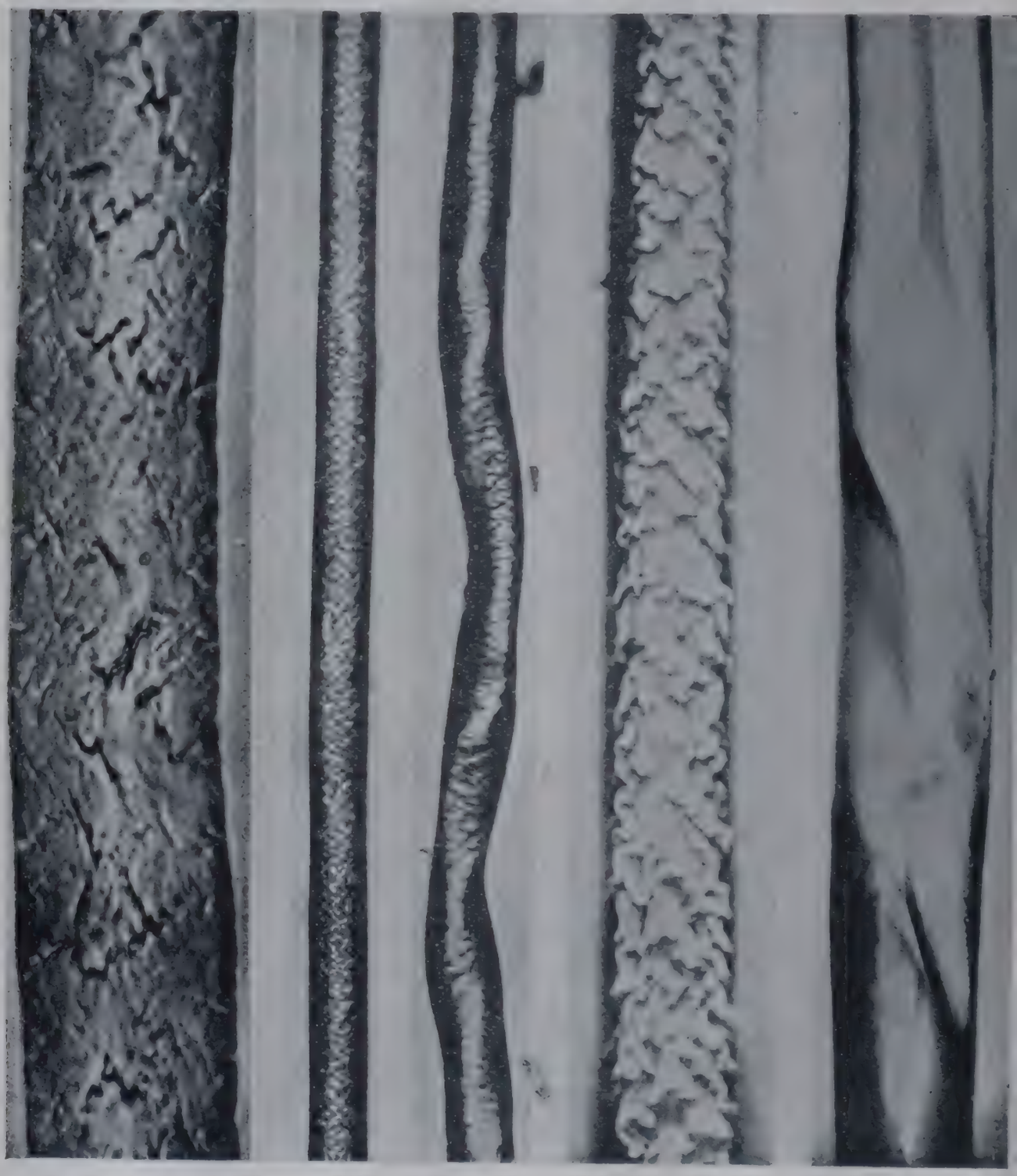

FIG. 42. — MODIFIED VISCOSE RAYON FIBERS (REUMUTH[60]).

Several viscose rayon staple fibers whose surfaces have been modified by appropriate stretching and setting during spinning.

Magnification × 650.

whereas the interior of the fiber varies depending on the conditions of manufacture. The rate of absorption and the amount of dyestuff taken up are intimately related to these differences in orientation.

It has been shown[63] that viscose rayons which have been attacked by microorganisms can be distinguished from unattacked viscose rayons by their appearance after staining with Congo red. This is possible because of

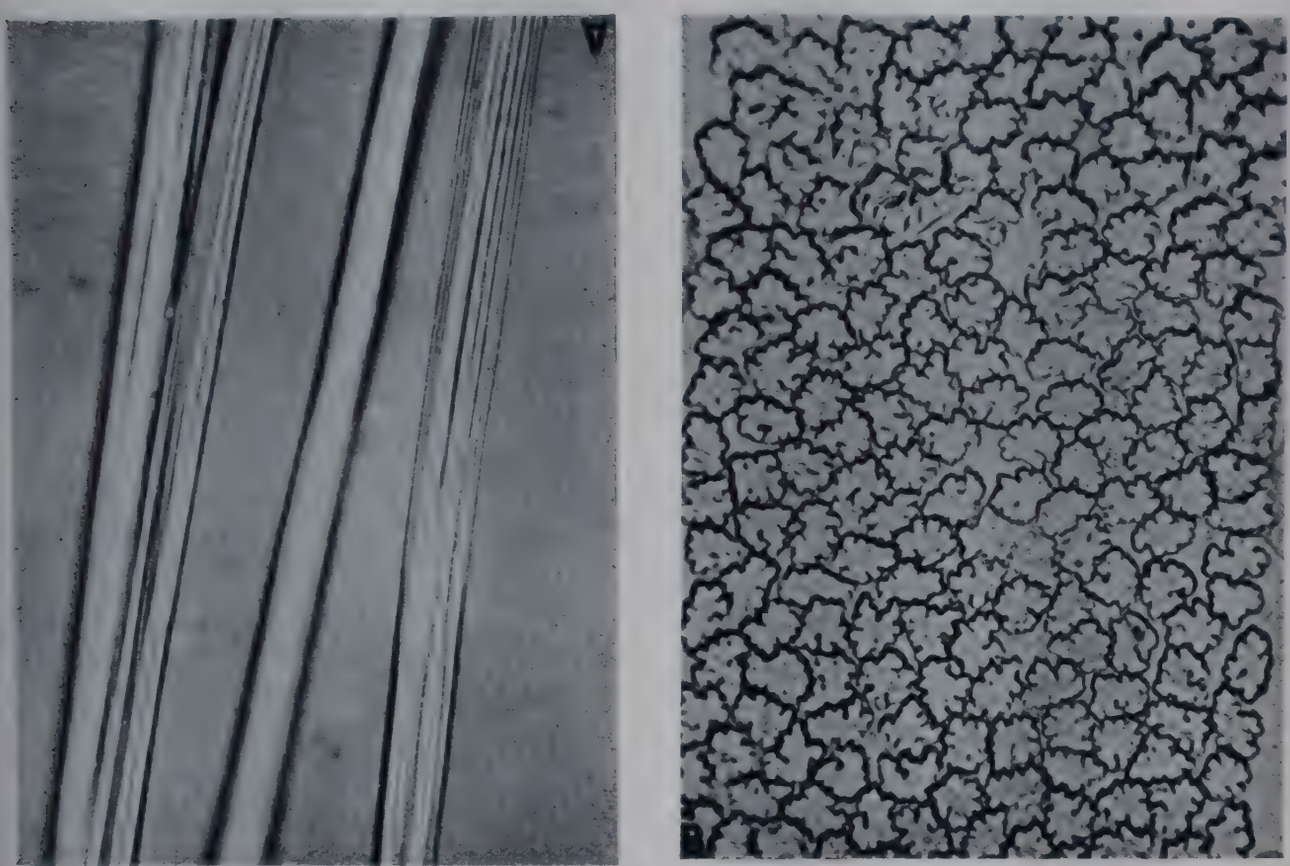

FIG. 43.—VISCOSE RAYON FIBERS.

A. Surface view. B. Cross sections.

Magnification × 220.

the skin which is present on viscose fibers and which is more resistant both to attack by bacteria and to staining. Damaged and stained fibers show deeply stained cracks and blotches where the skin has been removed, and where consequently the dye is able to penetrate more easily to the interior of the fibers.

Cuprammonium Rayon. Cuprammonium rayon has a smooth surface, an even diameter and usually no markings (Fig. 44A). Occasionally a few small hollow vesicles appear along the surface of the fiber but this is relatively infrequent. In cross section the fibers are found to be oval with an entire margin (Fig. 44B).

[63] T. F. Heyes and H. S. Holden, *J. Textile Inst.*, **23**, T82 (1932).

Cuprammonium fibers have no distinct differentiation in orientation of the surface layer such as that found in viscose fibers and hence are not

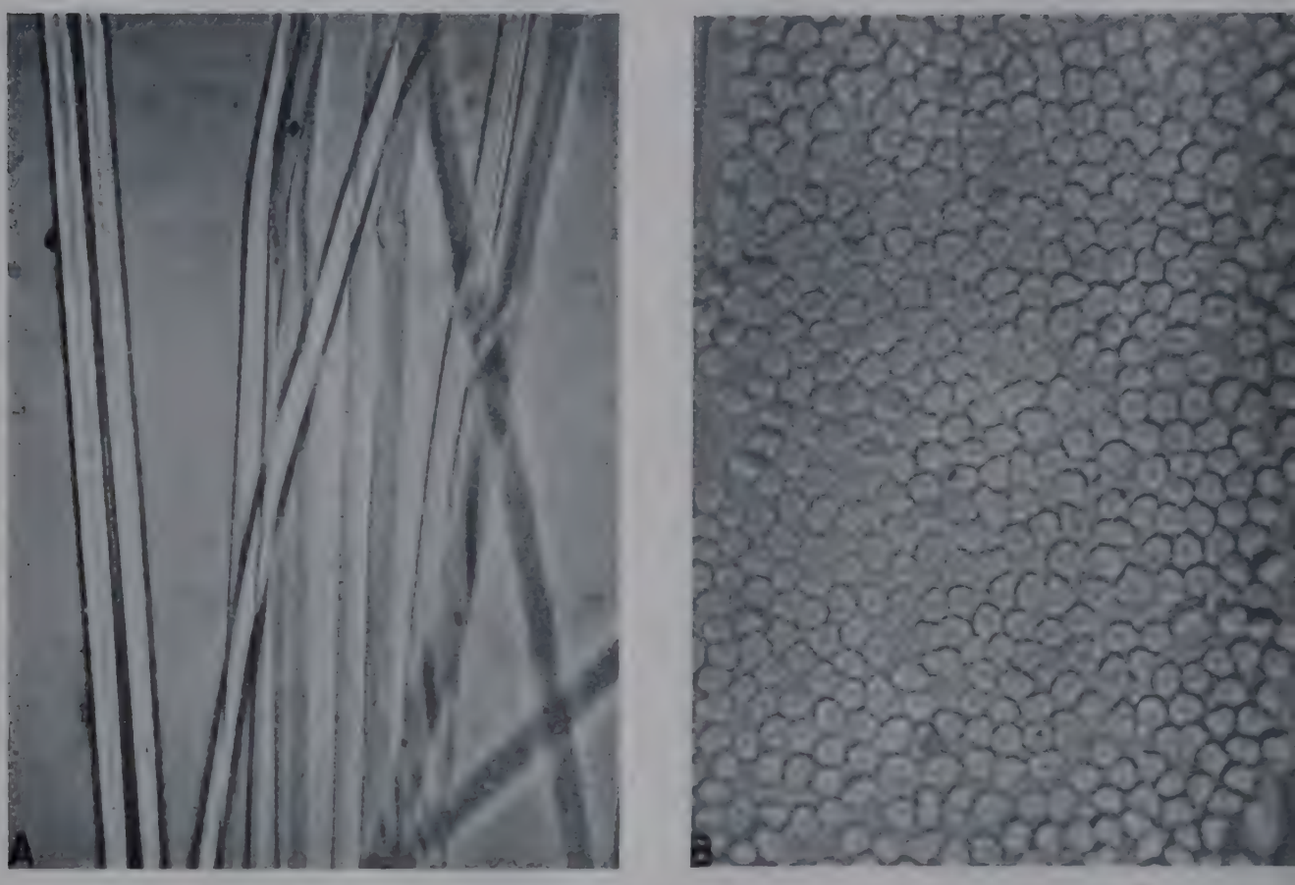

FIG. 44.—CUPRAMMONIUM RAYON FIBERS.
A. Surface view. B. Cross sections.
Magnification × 220.

so resistant to penetration and swelling which accompany dyeing. Accordingly, cuprammonium rayon generally dyes more uniformly than viscose rayon, which has a more oriented surface.

The appearance of various rayons in polarized light and between crossed nicols has been described by Lawrie[64] and by Herzog.[65] Since the thick parts of fibers give higher order colors than the thin parts, fibers with fluted surfaces can be distinguished from those which are uniform. Thus a striated viscose fiber is seen, for example, as a series of alternate higher and lower order colors corresponding to the striations, whereas an unstriated circular fiber such as cuprammonium rayon shows colors of progressively rising order from the edge to the center.

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[64] L. G. Lawrie, *J. Soc. Dyers Colourists*, **44**, 73 (1928).

[65] A. Herzog, *Die mikroskopische Untersuchung der Seide und der Kunstseide*. J. Springer, Berlin, 1924.

Acetate Rayons. Acetate rayon usually shows two to four deep striations in its surface (Fig. 45A). Correspondingly, cross sections have two to four large scallops which sometimes give the section a clover-leaf shape (Fig. 45B). Recently, acetate rayons exhibiting numerous serrations similar to viscose rayon have been produced.[10, 23]

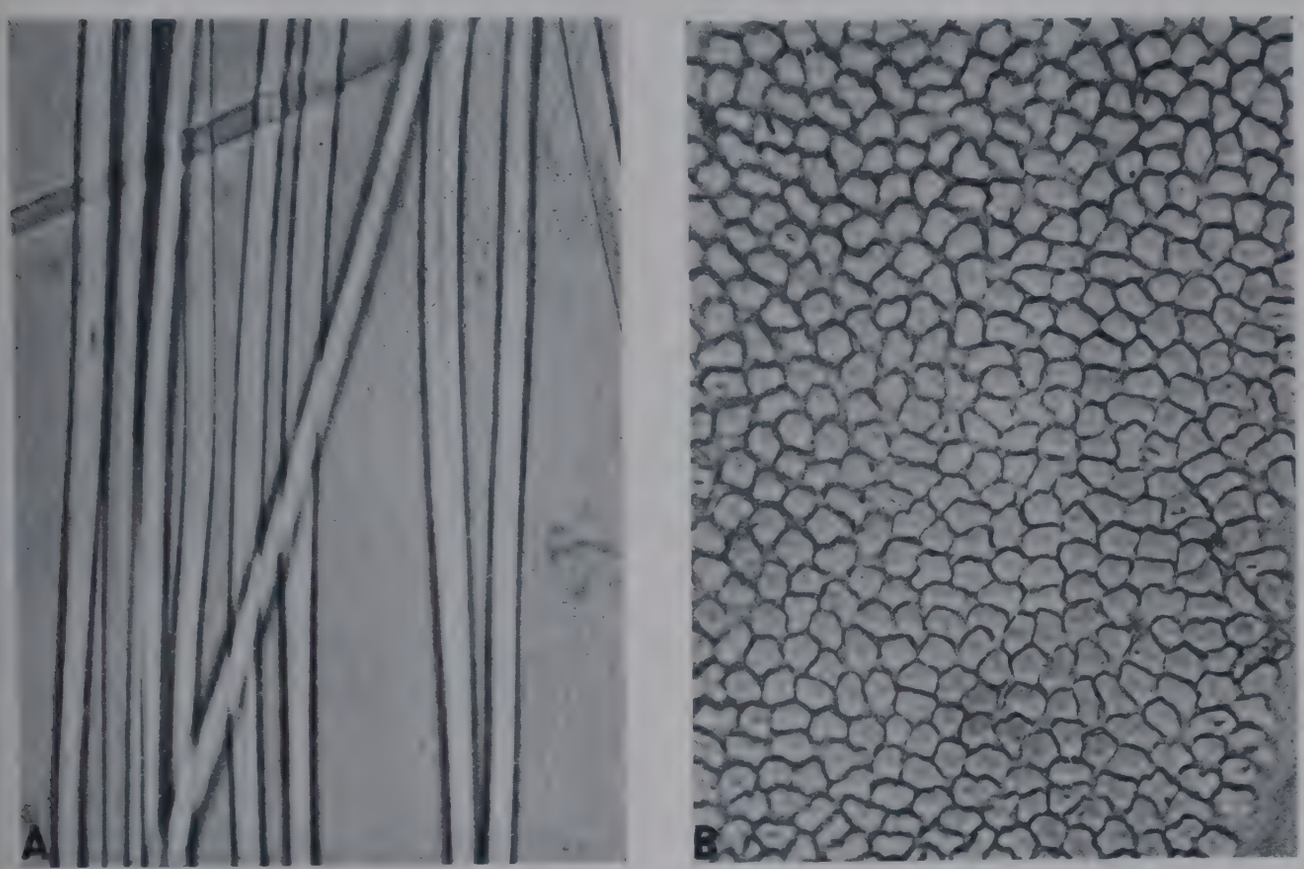

FIG. 45.—ACETATE RAYON FIBERS.

A. Surface view. B. Cross sections.

Magnification × 220.

Acetate rayon is sometimes partly hydrolyzed by a treatment with alkali which converts the cellulose acetate in the outer layer of the fiber into cellulose. This partial hydrolysis can be recognized by staining the fiber with cellulose and cellulose acetate dyes of different colors. These differences can be detected also by an examination of the fibers between crossed nicols. The acetate rayon has a low double refraction whereas hydrolyzed acetate rayon has a much higher value because of the skin effect of the regenerated cellulose formed by hydrolysis. In cross section these fibers are differentiated into an outer strongly anisotropic layer and an inner almost isotropic region.[57]

2. Investigation with the Electron Microscope†

Electron microscopy has now reached a stage of development in which it may be considered an available technique. Due chiefly to the advent of commercially made electron microscopes, there are now (early 1943) about three score of instruments in use on this continent. Although electron microscopy is still a new field and is, therefore, one not familiar to and understood by scientific workers in general, it seems inappropriate to use space in this book to discuss instruments and general techniques which are adequately treated elsewhere.[66, 67, 68] This brief discussion is limited to observations of fiber structure and behavior.

It must be emphasized that the examinations of cellulose fibers have, up to the present time, been exploratory in nature. Profound conclusions cannot be drawn. The results are interesting and stimulating to the imagination and, as the exploration continues, significant contributions to knowledge of fiber structure and behavior are certain to follow. The resolving power of electron microscopes under optimum operating conditions is of the order of 30 Å. Thus, structures composed of relatively few micelles are theoretically resolvable and it is intriguing, to say the least, to have fragments so nearly the size of the fundamental structural unit brought into the realm of the visible.

Ruska[69] examined cross sections of bast and cotton fibers. His sections were adequately thin for optical microscopic examination but were undesirably thick for study in the electron microscope. One micrograph of a bast fiber section shows evidence of a belt of fine pores at the periphery of the otherwise dense section. Micrographs of sections of cotton fibers show holes and openings in the fiber structure. Stereoscopic micrographs promise to be particularly helpful in the examination of such unavoidably dense specimens.

Ruska and Kretschmer[70] followed the chemical degradation of cotton fibers. Specimens treated with hydrochloric acid were reduced to very fine fibrils which those authors estimated to be of the order of 50 Å. in diameter.

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† Contributed by George R. Sears.

[66] M. von Ardenne, *Elektronen Übermikroskopie, Physik-Technik-Ergebnisse* J. Springer, Berlin, 1940.

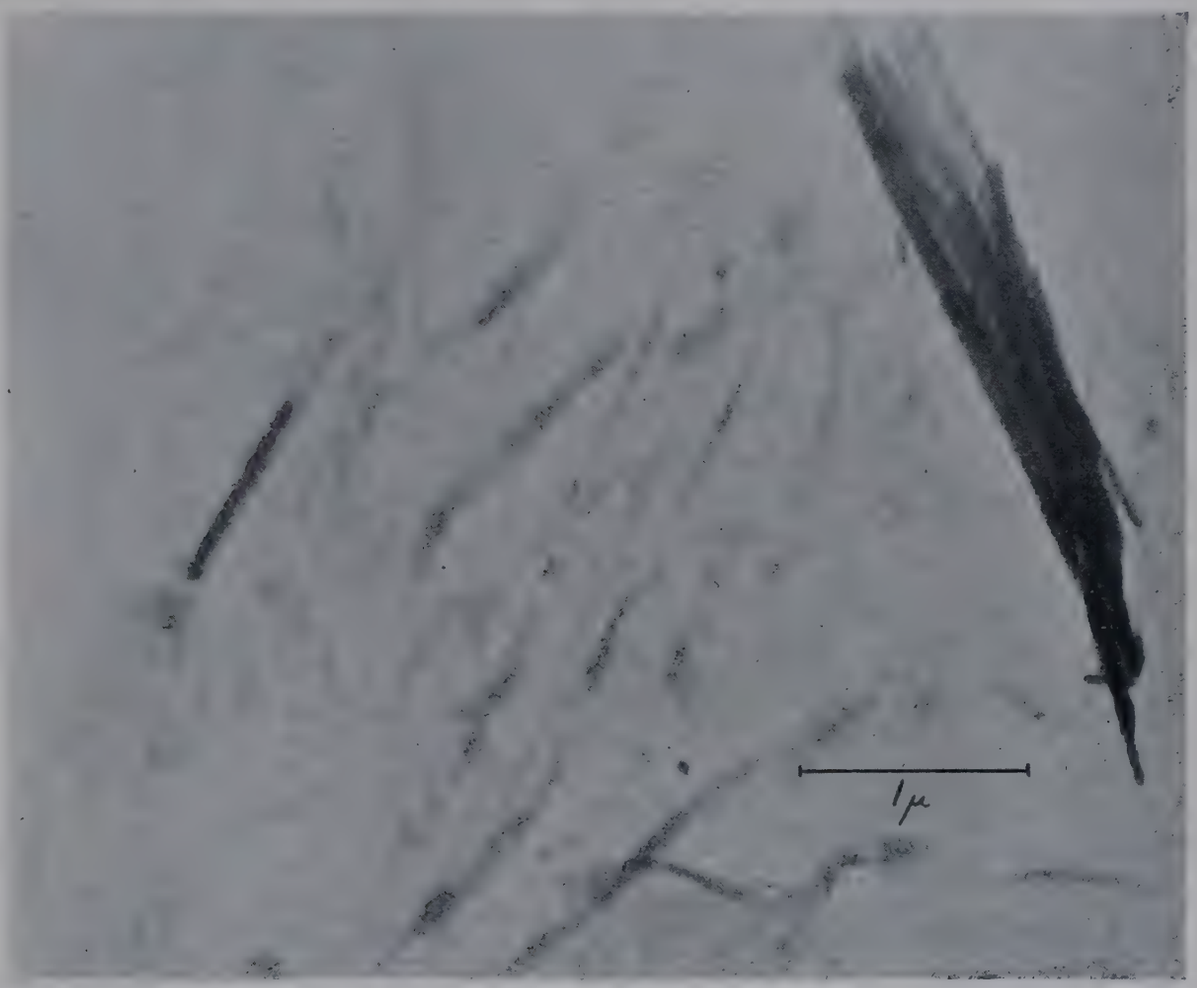
[67] T. F. Anderson, *The Study of Colloids with the Electron Microscope*, in E. O. Kraemer, *Advances in Colloid Science*. Interscience, New York, 1942.

[68] E. F. Burton and W. H. Kohl, *The Electron Microscope*. Reinhold, New York, 1942.

[69] H. Ruska, *Kolloid-Z.*, **92**, 276 (1940).

[70] H. Ruska and M. Kretschmer, *Kolloid-Z.*, **93**, 163 (1940).

Berkley and Greathouse[71] used an ingenious dissection technique in examining the fine structure of cotton fibers. The fibers were severely irradiated with a quartz mercury arc and the embrittled fibers were ground to a powder on a microscope slide with the use of a glass rod. The electron micrograph of a specimen obtained from this powdered material is presented in Figure 46 and shows rodlike particles, separated and in bundles, having diameters of 150–200 Å. and lengths of 10,000–15,000 Å. This technique



Courtesy of E. E. Berkley and G. A. Greathouse

FIG. 46.—ELEMENTS OF COTTON FIBER OBTAINED BY SEVERE ULTRAVIOLET IRRADIATION AND SUBSEQUENT GRINDING.

constitutes a significant variation from the previously used chemical methods of disintegrating fibers.

Preliminary studies of papermaking fibers[72, 73] show that cotton, wood, and bast fibers develop fine fibrils when beaten or mechanically treated in water. The fibrillation of a fragment of southern pine kraft fiber from a

[71] E. E. Berkley and G. A. Greathouse, private communication.

[72] G. R. Sears and E. A. Kregel, *Paper Trade J.*, **114**, 43 (Mar. 19, 1942).

[73] Inst. of Paper Chemistry, unpublished work.

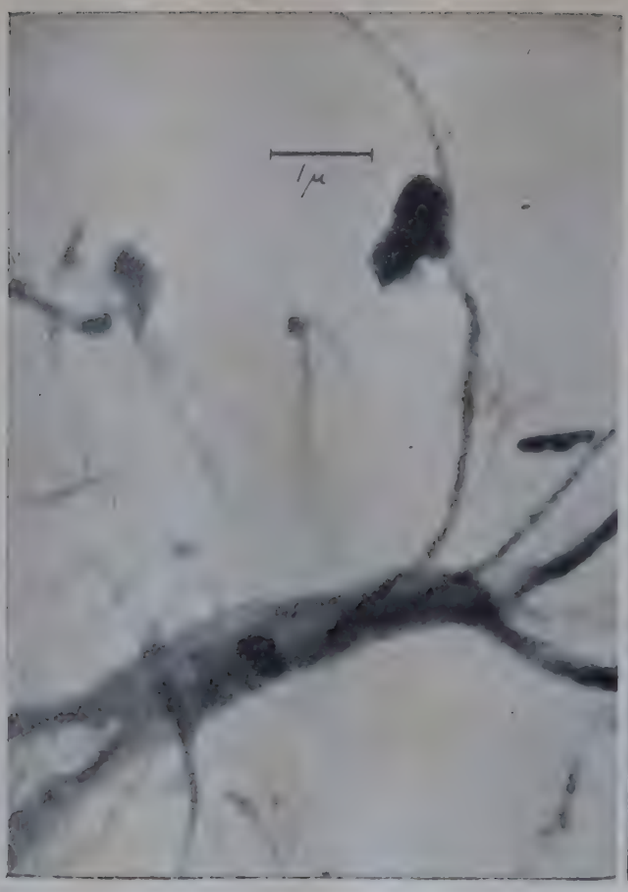


FIG. 47.—FRAGMENT OF WOOD-PULP FIBER SHOWING FIBRILLATION.

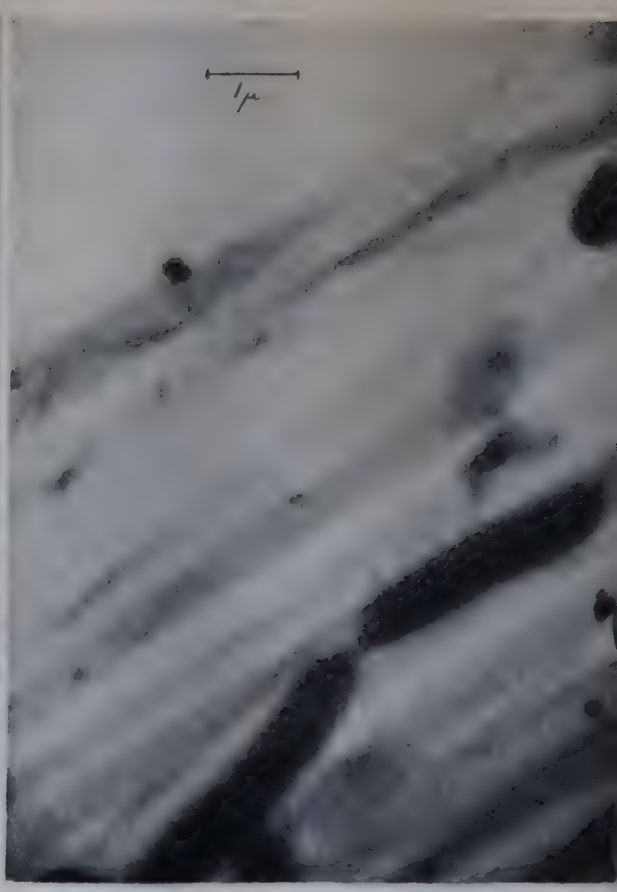


FIG. 48.—RIBBONLIKE STRUCTURES NOTED IN LIGHTLY BEATEN KRAFT PULPS.

FIG. 49.—LAMINAE OF UNSEPARATED FIBRILS FREQUENTLY FOUND IN CHEMICAL WOOD PULPS.

FIG. 50.—TYPICAL CONTOUR OF UNBEATEN FIBER IN CHEMICAL WOOD PULP.

well-beaten stock is illustrated in Figure 47. The finest fibrils found in beaten papermaking fibers are less than 300 Å. in diameter but do not seem to be as small in diameter as those found by Ruska and Kretschmer in chemically degraded cotton fibers. Many of the fibrils are more than 15 μ

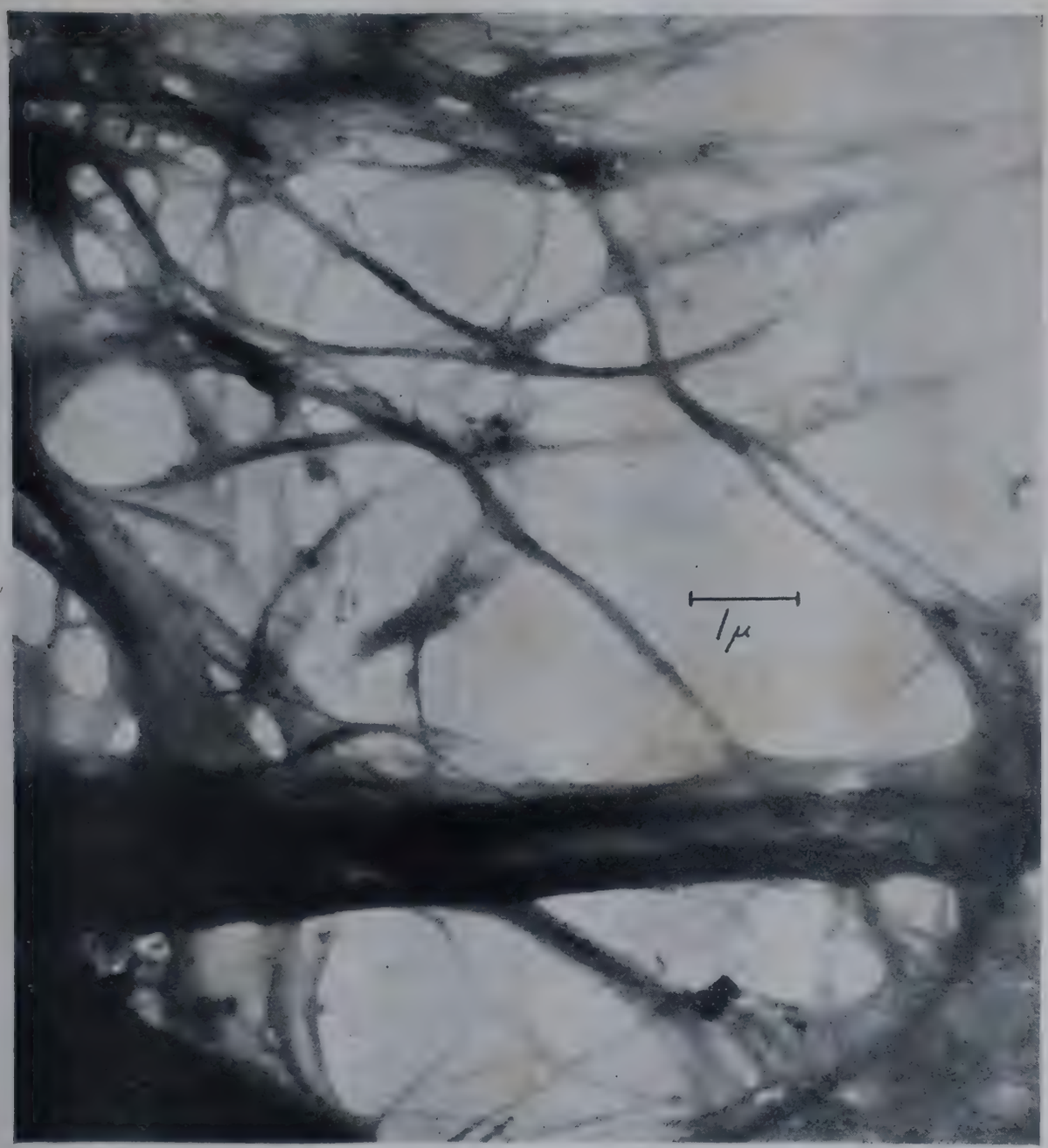


FIG. 51.—FIBRILLATION OF COTTON FIBERS IN PAPERMAKING RAG STOCK.

long. Another type of structure noted in lightly beaten kraft pulps is the ribbon-like form presented in Figure 48. The dark sausage-like objects are bacteria. Frequently, relatively large sheets or laminae of incompletely separated fibrils are observed. Figure 49 shows two accidentally superposed layers and illustrates that type of structure; this particular

specimen was part of a sulfite fiber. Upon additional mechanical treatment these laminae break down into separated fibrils. Unbeaten wood or bast fibers are too thick to show evidence of internal structure or arrangement and usually their contours give no indication of the underlying fibrils. The contour presented in Figure 50 may be considered typical.

The fibrillation found in rag stock is essentially of the same degree of fineness. However, the fiber fragments appear more membranous than do the fragments of wood fibers. The junctions of fibrils and the holes which appear in the larger elements are suggestive of the results of tearing and rupturing a continuous structure. Figure 51 is a typical micrograph of the fine fraction of a moderately beaten rag stock. The difference in the appearance of the fragments and fibrils of cotton and wood fibers seems significant and needs to be interpreted.

It is tempting to conjecture regarding the future contributions of electron microscopy to fiber structure, but it is futile to try to suggest the directions in which the contributions will be made. The importance of the findings will depend not only upon the constant application of the instrument to the many problems in the field but upon the ingenuity of the investigators in selecting and preparing specimens.

EDITOR'S NOTE. Since the field of electron microscopy is so new, a short bibliography of literature references more recent than those included in this article is appended:

1. H. Jentgen, *Jentgen's Kunstseide u. Zellwolle*, **23**, 76 (Mar., 1941); *Bull. Inst. Paper Chem.*, **12**, 389 (Aug., 1942); *Chem. Abstracts*, **36**, 4331 (1942).

2. K. Hess, H. Kiessig, *et al.*, *Z. physik. Chem.*, **B49**, 64 (1941).

3. E. Franz, L. Wallner, *et al.*, *Kolloid-Z.*, **97**, 36 (1941); *Chem. Abstracts*, **36**, 7304 (1942).

4. E. Kuhn, *Melliand Textilber.*, **22**, 249 (1941); *Rayon Textile Monthly*, **23**, 101 (1942).

5. H. Mahl, *Kolloid-Z.*, **96**, 7 (1941); *Chem. Abstracts*, **36**, 6075 (1942).

6. W. Wergin, *Kolloid-Z.*, **98**, 131 (1942); *Chem. Abstracts*, **36**, 5639 (1942).

7. O. Eisenhut and E. Kuhn, *Chemie*, **55**, No. 25/26, 198 (June 3, 1942); *Bull. Inst. Paper Chem.*, **13**, 147 (Dec., 1942).

8. L. Wallner, *Melliand Textilber.*, **23**, 261 (1942); *Bull. Inst. Paper Chem.*, **13**, 147 (Dec., 1942).

9. C. J. Burton, R. B. Barnes, and T. G. Rochow, *Ind. Eng. Chem.*, **34**, 1429 (1942).

10. R. B. Barnes and C. J. Burton, *Ind. Eng. Chem.*, **35**, 120 (1943).

11. A. Hamann, *Kolloid-Z.*, **100**, 248 (1942); *Chem. Abstracts*, **37**, 1597 (1943).

12. K. Hess, E. Steurer, *et al.*, *Kolloid-Z.*, **98**, 148 (1942); *Chem. Abstracts*, **36**, 5581 (1942).

13. E. H. Lundgren, *Tek. Tid.*, **71**, Uppl. A-C, *Kemi*, 29 (1941); *Chem. Abstracts*, **35**, 5385 (1941).

14. F. E. Wallner and E. Schiebold, *Kolloid-Z.*, **97**, 36 (1941).

15. L. W. Wallner, *Melliand Textilber.*, **23**, 158 (1942); *Chem. Abstracts*, **37**, 4576 (1943).

D. MERCERIZATION

E. I. VALKO

Mercerization is the name used in the textile industry for the treatment of cotton yarn or fabric with concentrated aqueous caustic solution. The process dates from 1844, when John Mercer,[1] upon filtering concentrated caustic soda through a cotton cloth, observed that the cotton swelled considerably and showed somewhat modified properties even after the caustic had been removed by washing. The fabric shrank, its tensile strength increased, and it acquired a higher power to absorb dyestuffs. Caustic potash, sulfuric acid of certain concentrations, and aqueous zinc chloride were found to have the same effects on the cloth as had sodium hydroxide, and Mercer took out a patent covering the use of all of these compounds to modify the physical properties of cellulose.[2] Mercerization developed into an important industrial process following the observation of Horace Lowe, nearly half a century later, that upon treating cotton cloth with caustic soda under tension in order to prevent shrinkage, the cotton acquired a silk-like luster.[3]

The present use of the mercerizing process aims almost always at increasing the luster of cotton. The comparatively low cost of the process promoted its wide use, and mercerization has retained its place in the textile industry even after the growth of rayon manufacture, perhaps because it combines with the production of the silky luster a retention of the strength of the native fiber.

During the century which has elapsed since Mercer's discovery, several hundred scientific investigations have been carried out on mercerizing. They have substantially enriched the knowledge of fiber structure, but they have influenced industrial practice only slightly. The literature has been

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[1] E. A. Parnell, *The Life and Labours of John Mercer*. Longmans, Green & Co., London, 1886.

[2] J. Mercer, Brit. Patent 13,296 (Oct. 24, 1850).

[3] H. A. Lowe, Brit. Patent 4452 (Dec. 22, 1890).

reviewed by Clibbens,[4] Valko,[5] and Marsh,[6] and a bibliography has been compiled by Edelstein and Cady.[7]

1. Effects of Mercerization

Our knowledge of mercerization has come from the results of investigations concerned with: (a) the mechanism of the chemical interaction of cellulose and alkalies; (b) the physical changes of the fibers during the treatment with the caustic and during the subsequent washing; and (c) the permanent changes in the properties of the fibers produced by the mercerizing process. A study of all three is necessary for an understanding of the process, but, since the first two of these will be presented at length in Chapter VIII, D on "Alkali and Other Metal Derivatives of Cellulose," only a brief summary of them will be given here.

(*a*) *Mechanism of Chemical Interaction of Cellulose and Alkalies*

Cellulose combines with sodium hydroxide to form several modifications of alkali cellulose. The compounds can be quite definite, but the amount of alkali bound by a sample of cellulose, and the amount of water bound by the compounds, varies with the alkali concentration, the temperature, and other factors.

The reaction of cellulose with caustic produces heat, which has been successfully calculated by considering it to be the sum of three components: positive heat of dissociation of a weak acid; negative heat of neutralization, *i. e.*, heat of formation of water; and negative heat of dilution of the alkali.

The cellulose-alkali compounds hydrolyze on washing with water, and the caustic can be easily and completely removed.

(*b*) *Physical Changes of Fibers during Treatment with Caustic and during Subsequent Washing*

The two important changes in the fiber during the alkali treatment are an increase in its diameter ("swelling") and a decrease in its length ("shrinking"). Both swelling and shrinking pass through maxima when plotted against alkali concentration. When sodium hydroxide is the alkali, these maxima tend to fall at the same concentration, but they do

[4] D. A. Clibbens, *J. Textile Inst.*, **14**, T217 (1923).

[5] E. Valko, *Kolloidchemische Grundlagen der Textilveredlung*. J. Springer, Berlin, 1937.

[6] J. T. Marsh, *Mercerizing*. Chapman & Hall, London, 1941.

[7] S. M. Edelstein and W. H. Cady, *Am. Dyestuff Reptr.*, **26**, P447 (1937).

not coincide when other alkalies are used. The amount of swelling at a given alkali concentration depends greatly on the external surface of the sample. For instance, "scoured" cotton (cotton which has been boiled in dilute alkali) swells more than does raw or "gray" cotton, while "rubbed" fibers (those from which the outer layer has been removed with fine emery paper) swell even more[8] (Fig. 52). Regenerated cellulose swells the most. The swelling can be explained by three different but somewhat related theories. The first is that the fiber surface acts as a semipermeable mem-

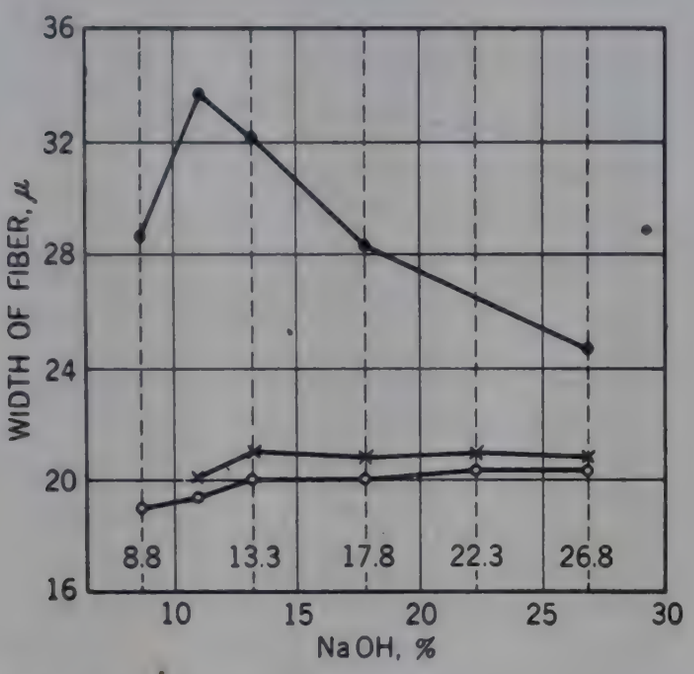

FIG. 52.—INCREASE OF THE WIDTH OF COTTON FIBERS IN NaOH SOLUTIONS (CALVERT[8]).

Lower curve: raw hairs.
Middle curve: scoured hairs.
Upper curve: rubbed hairs.

brane inside which osmotic pressure is built up as a consequence of the Donnan equilibrium or by the solution of cellulose chains in the alkali used. The second theory is that hydration of the alkali cellulose causes the effect. The third is that the swelling is caused by the electrostatic repulsion between the cellulose particles, which are charged as a result of ionization. The amount of shrinkage a fiber undergoes on mercerization is also determined to some extent by the external surface. The shrinkage can be prevented by application of tension to the fiber. Because the shrinkage remains after the alkali is washed out, in contrast to the swelling, it will be discussed below in the group of the permanent changes.

[8] M. A. Calvert, *J. Textile Inst.*, 21, T293 (1930).

(c) *Permanent Changes Produced by Mercerization in Properties of Fibers*

The changes which the mercerizing process causes in cellulosic materials fall into four categories. These comprise: the changes in the cellulose molecules themselves; those produced in the intermolecular structure of cellulose crystallites; those produced in the distribution of crystallites and amorphous material in the cellulosic material; and, finally, those produced in the microscopic structure of the fibers.

Changes Produced in the Cellulose Molecules. There is no reason to assume any *structural difference between the single polymeric molecules* of native and of mercerized cellulose. The interpretations of the x-ray

TABLE 1

EFFECT OF MERCERIZING ON THE CHEMICAL PROPERTIES OF SCOURED COTTON (RIDGE, PARSONS, AND CORNER[9])

Variety	Fluidity		Copper number		Methylene blue number		Loss of wt. in alkali boil, %	
	Native	Mercerized	Native	Mercerized	Native	Mercerized	Native	Mercerized
Egyptian Sakel	3.68	3.70	0.01	0.01	1.17	0.96	1.32	1.23
Egyptian Uppers	3.38	3.34	0.01	0.01	1.10	0.95	1.20	1.31
Tanguis	3.47	3.42	0.015	0.01	1.24	1.09	0.84	1.28
Arizona	3.87	3.67	0.01	0.01	1.35	0.98	1.37	1.30
Peru Mitafifi	3.52	3.21	0.01	0.01	1.03	0.88	0.88	1.0

diagrams of the crystalline part of both modifications were carried out under the assumption that the molecular structure is the same in both. The only other possible molecular change is depolymerization. However, as was demonstrated, for instance, by Ridge, Parsons, and Corner,[9] all the properties of cotton which depend on the extent of the degradation remain essentially unchanged by the mercerizing process. Table 1 shows the results obtained on scoured cotton yarn which was mercerized with a 9 *N* NaOH solution. The measurements were carried out under strictly identical conditions.

Staudinger,[10] through the use of his viscosity method, found that a cotton cellulose was changed on mercerization from a degree of polymerization (D.P.) of 3000 to a D.P. of 2000. This change is inappreciable, since

[9] B. P. Ridge, H. L. Parsons, and M. Corner, *J. Textile Inst.*, 22, T117 (1931).
[10] H. Staudinger and A. W. Sohn, *J. prakt. Chem.*, **155**, 177 (1940).

a depolymerization to a D.P. of 500 would still have left the mechanical properties of the cellulose practically unchanged.

Changes Produced in the Crystallites. X-ray examination of the native and of the mercerized fiber gives evidence for a change of crystalline form produced by mercerization, and it has been proved by Meyer and Badenhuizen[11, 12] and Kubo[13] that this change is reversible. The crystalline structures of native and of regenerated cellulose are, therefore, polymorphic. The question as to which form is more stable at room temperature cannot be answered as yet, but the direct transformation of mercerized into native cellulose indicates that at higher temperatures the native is the more stable form. There has been a tendency, in theoretical treatises on mercerization, to attribute a great significance to the transformation of the crystal forms, but it seems more correct to regard it as an interesting, yet merely accessory, phenomenon connected with the mercerizing process. There are very few properties of mercerized cellulose, and none of technical significance, for which the difference between the crystal structure of native and of mercerized cellulose could be held responsible.

Changes in Distribution of Crystallites and Amorphous Material. All of the technically important changes in fiber properties which are produced by the mercerizing process, with the noteworthy exception of the most important one, the increase in luster, can be traced to two intermicellar changes. These two changes are the decrease in the amount of crystalline material, and the change in orientation of the crystallites.

No comparative quantitative measurement of the sharpness of x-ray diagrams of native and mercerized cellulose has been reported. However, measurement of the x-ray diagrams of rayon (from regenerated cellulose) which is known to show the peculiarities of mercerized cellulose in an exaggerated degree, showed a decrease in the sharpness of the diffraction rings, giving a quantitative indication of a decrease in the size of the crystallites or an increase in the number of distortions or discontinuities in the lattice structure.

It was observed that the scattering was more intense and the rings were more diffuse for rayon than they were for native cellulose. This finding indicates that by the mercerizing process the amount of amorphous material is increased at the expense of the crystalline material. Furthermore, the x-ray diagrams proved that when the mercerization is carried out without tension, the orientation of the crystallites decreases substan-

[11] K. H. Meyer and N. P. Badenhuizen, *Nature*, **140**, 281 (1937).
[12] K. H. Meyer, L. Misch, and N. P. Badenhuizen, *Helv. Chim. Acta*, **22**, 59 (1939).
[13] T. Kubo, *Kolloid-Z.*, **93**, 338 (1940); *Z. physik. Chem.*, **A187**, 297 (1940).

tially. When the mercerizing is carried out under tension, the degree of orientation is retained or even increased.[14]

Effects of the Decrease in Amount of Crystalline Material. The decrease in the amount of crystalline material and increased separation of the cellulose

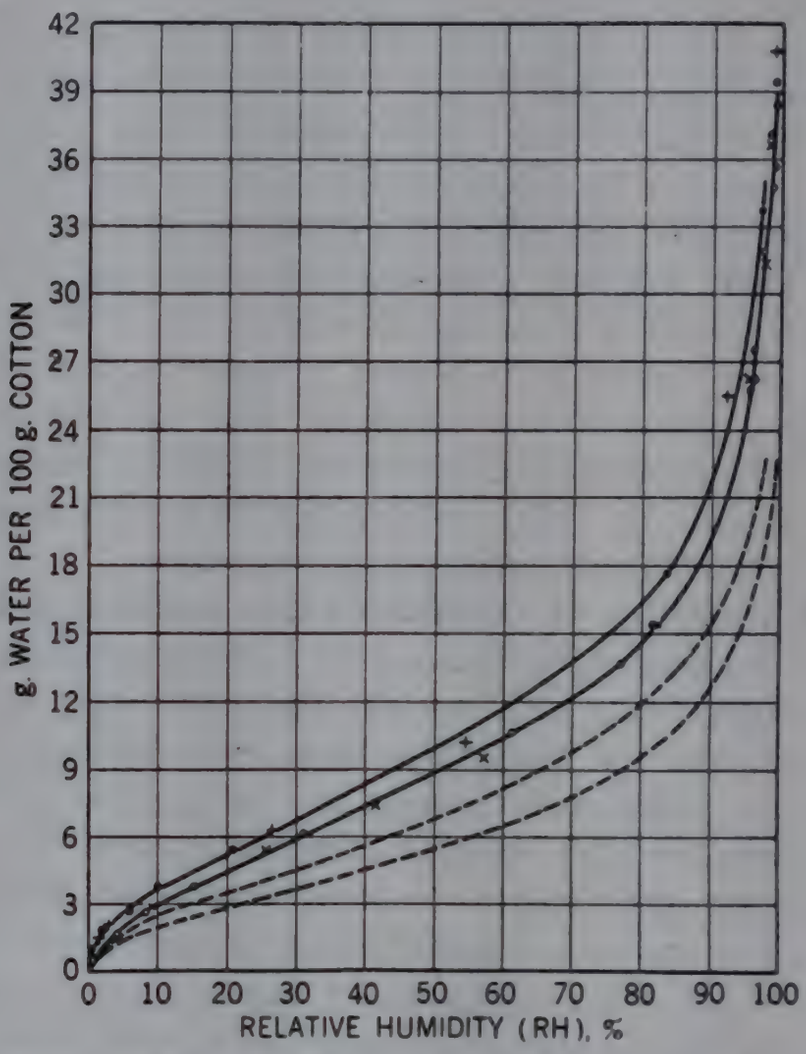

FIG. 53.—ABSORPTION OF WATER BY NATIVE AND BY MERCERIZED COTTON (URQUHART AND WILLIAMS[16]).

Curves (from top to bottom): mercerized cotton, desorption; mercerized cotton, adsorption; native cotton, desorption; native cotton, adsorption. Points refer to cotton, the mercerization of which was carried out with 15% NaOH solution; crosses refer to cotton, the mercerization of which was carried out with 28% KOH solution.

chains result in the decreased density, increased adsorption, and increased reactivity of the mercerized fibers. The density measurements were carried out by Davidson,[15] who used the pycnometric method with helium, water,

[14] G. L. Clark, *Ind. Eng. Chem.*, **22**, 474 (1930).

[15] G. F. Davidson, *J. Textile Inst.*, **18**, T175, T275 (1927).

[16] A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, **16**, T155 (1925); **18**, T55 (1927).

and toluene as media. Results obtained are included in Table 8 (p. 407) of Section G of this chapter. The values obtained in helium were regarded as truly representing the specific volume, and, from the differences in the apparent values in helium and in water, the decrease in specific volume caused by the adsorption of water (the "contraction volume") was calculated. The average decrease was 0.018 cc. for 1 g. for scoured cotton and 0.023 cc. for 1 g. for mercerized cotton. This is in accord with the fact that mercerized cotton absorbs more water than does native cotton.

Mercer recognized that cotton becomes more hygroscopic after treatment with caustic, but exact measurements under strictly comparable conditions were carried out for the first time by Urquhart and Williams.[16] In Figure 53 are presented the percentages of water sorbed at various relative humidities by native (kier-boiled) cotton and by the same cotton after mercerization without tension. The ratio of the water contents of mercerized and native cotton is nearly constant for all relative humidities. In this particular case, the mercerized cotton takes up about 1.5 times as much water as does native cotton. The ratio depends on the concentration of the mercerizing solution and upon the tension applied during the treatment (Fig. 54).

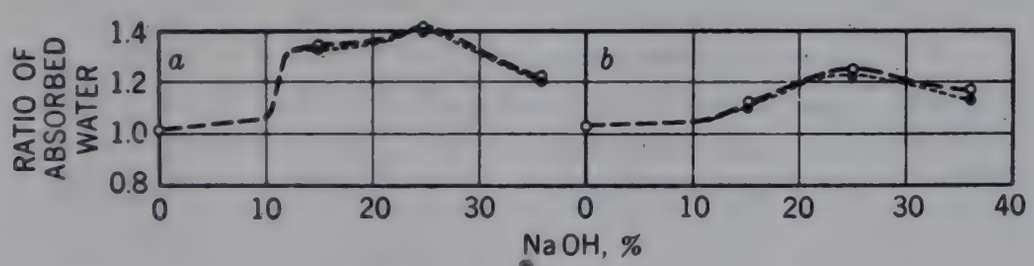

FIG. 54.—RATIO OF THE AMOUNT OF WATER ABSORBED BY COTTON WHICH WAS TREATED WITH NaOH SOLUTIONS OF VARIOUS CONCENTRATIONS, (*a*) WITHOUT TENSION AND (*b*) UNDER TENSION, TO THE AMOUNT OF WATER ABSORBED BY UNTREATED COTTON (URQUHART AND WILLIAMS[16]).

– – – – – – – – Adsorption.
- - - - - - - - - - Desorption.

Another method of measuring water adsorption was used by Champetier[17] and Tankard[18] who measured the increase in concentration of an aqueous thiosulfate solution caused by the removal of water by mercerized and by native cotton which were soaked in it. They found the increase to be about twice as great for the former as for the latter.

Alkaline substances, such as sodium hydroxide, barium hydroxide, and

[17] G. Champetier, *Compt. rend.*, **195**, 280 (1932).
[18] J. Tankard, *J. Textile Inst.*, **28**, T263 (1937).

copper (from cuprammonium hydroxide), are also adsorbed from aqueous solution more strongly by mercerized cotton than by native. As the concentration of these bases increases, the difference in adsorption disappears gradually as the fiber is transformed from the native into the mercerized state. The ratio of the amounts of Na^+ ion adsorbed from 0.5 *N* NaOH solution by mercerized and by native cellulose, and the similar ratios of Ba^{++} ion adsorption from 0.2 *N* $Ba(OH)_2$ were used by Neale[19] for measuring the effects produced by mercerizing cotton under various conditions (Table 2).

TABLE 2

RATIOS OF THE ALKALI ADSORPTION OF COTTON YARN MERCERIZED WITH 25% NaOH TO THAT OF NATIVE COTTON (NEALE[19])

Cotton		Dried at room temperature		Dried at 110°C. for 6 hrs.	
		Na^+ ion ratio	Ba^{++} ion ratio	Na^+ ion ratio	Ba^{++} ion ratio
Scoured and then mercerized	Loose (about 15% shrinkage)	2.55	2.70	2.27	2.50
	Loose and restretched	2.07	2.10	1.93	1.98
	No shrinkage allowed	1.96	2.05	1.89	1.99
	Cloth mercerized loose	2.13	..	..	..
Mercerized in the "gray" state and then scoured	Loose (about 15% shrinkage)	2.09	2.20	1.84	1.97
	Loose and restretched	1.76	1.79	1.76	1.83
	No shrinkage allowed	1.68	1.73	1.69	1.75

TABLE 3

AMOUNT OF BENZOPURPURIN 4 B ADSORBED BY NATIVE COTTON AND BY COTTON TREATED WITH NaOH SOLUTIONS OF DIFFERENT STRENGTHS (KNECHT[20])

Concentration of NaOH, %	Dye adsorbed by cotton, g. per 100 g.	Concentration of NaOH, %	Dye adsorbed by cotton, g. per 100 g.
0.00	1.77	20.5	3.27
4.5	1.88	22.5	3.38
8.5	2.39	25.0	3.50
11.0	2.57	27.0	3.56
13.5	2.95	29.0	3.60
15.5	3.02	31.5	3.60
17.5	3.15		

[19] S. M. Neale, *J. Textile Inst.*, **22**, T320, T349 (1931).
[20] E. Knecht, *J. Soc. Dyers Colourists*, **24**, 68, 107 (1908).

Another effect of the mercerization process on the fiber is that the adsorptive power for dyes is increased. Knecht[20] investigated systematically the influence of the concentration of the mercerizing solution (Table 3), of the tension applied during the treatment (Table 4), and of the drying operation (Table 5), on dye adsorption. The effect of drying noticed here is in agreement with the observation of Urquhart, Bostock, and Eckersall[21] that the fibers exhibit a much higher sorption of water immediately after mercerizing and washing than after the subsequent drying. It can be assumed that the factor responsible for this phenomenon is a delayed recrystallization of part of the amorphous cellulose.

TABLE 4

AMOUNT OF BENZOPURPURIN 4 B ADSORBED BY NATIVE AND BY MERCERIZED COTTON (KNECHT[20])

Cotton	Dye adsorbed by cotton, g. per 100 g.	
	Bleached	Unbleached
Native	1.50	1.55
Mercerized under tension	2.86	2.90
Mercerized without tension	3.54	3.39

TABLE 5

AMOUNT OF DYE ADSORBED BY COTTON (KNECHT[20])

Cotton	Dye adsorbed by cotton, g. per 100 g.	
	Benzopurpurin 4 B	Chrysophenin
Mercerized and dyed without drying	2.49	0.97
Mercerized and air-dried before dyeing	1.57	0.77
Mercerized and dried at 110°C. before dyeing	1.27	0.54
Native	0.80	0.31

Boulton and Morton[22] found that the speed of adsorption of dyes, as measured by the time which is necessary to reach the half value of the adsorption equilibrium, is greatly increased by mercerizing. For example, two samples of raw cotton gave half-time values of 1.1 and 1.4 minutes with Sky Blue FF, a substantive dye, under the particular conditions of their experiments. After the cottons were mercerized under tension, the values were 0.25 and 0.35 minutes, respectively.

[21] A. R. Urquhart, W. Bostock, and N. Eckersall, *J. Textile Inst.*, **23**, T135 (1932)

[22] J. Boulton and T. H. Morton, *J. Soc. Dyers Colourists*, **56**, 145 (1940).

One view concerning dye adsorption which cannot be explained by th increase in amorphous material is that less dye is required by mercerized cotton to produce a given shade than is required by raw cotton. Thi opinion is held by many workers in spite of the fact that Hübner[23] dis missed the possibility some thirty years ago and that no quantitative test have since been reported. It is not unlikely that such an effect is produced

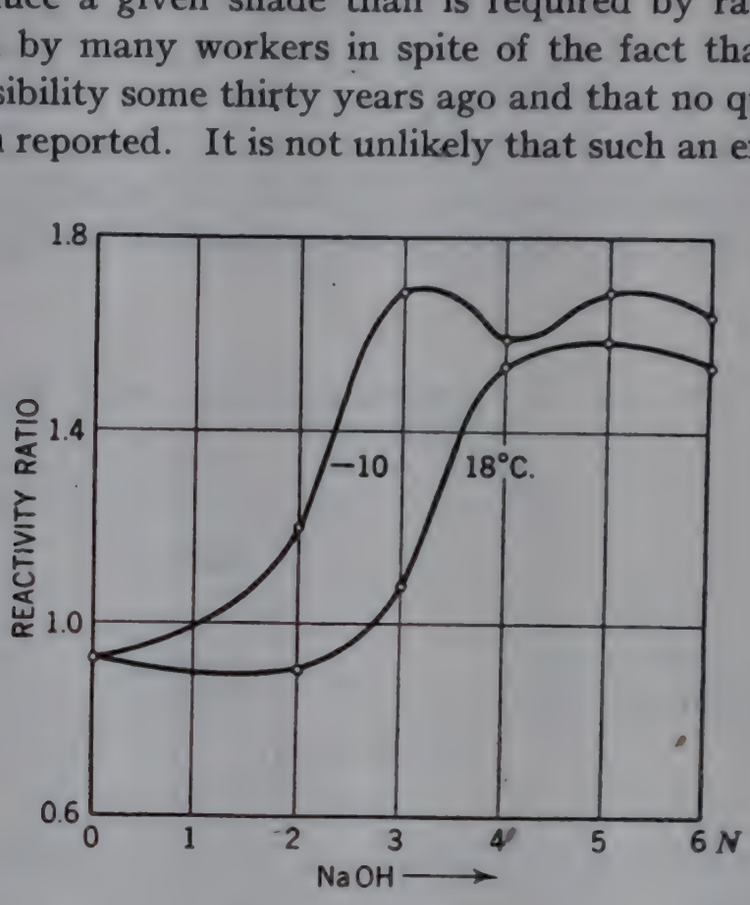

FIG. 55.—REACTIVITY RATIO OF COTTON TREATED WITH NaOH SOLUTIONS OF VARIOUS CONCENTRATIONS AT 18°C. AND AT −10°C. TO THAT OF NATIVE COTTON (BIRTWELL, CLIBBENS, GEAKE, AND RIDGE[25]).

by the mercerization process, but the explanation for it would seem to lie in the increased luster of the fiber, which would cause a higher brilliance of the color.

The increased reactivity of mercerized cellulose, caused by the increase in amount of amorphous material, is shown by the fact that the rates of attack of hydrolyzing and oxidizing agents on it are greater than they are on native cellulose. Schwalbe[24] suggested the use of the copper number, obtained from various celluloses after treatment of 15 minutes with 5% H_2SO_4 solution, as a means of characterizing the reactivity of a fiber, and

[23] J. Hübner, *J. Soc. Chem. Ind.*, **27**, 105 (1908).

[24] C. G. Schwalbe, *Z. angew. Chem.*, **22**, 197 (1909).

[25] C. Birtwell, D. A. Clibbens, A. Geake, and B. P. Ridge, *J. Textile Inst.*, **21**, T85 (1930).

he found that this value is greatly increased by the mercerization process. Birtwell, Clibbens, Geake, and Ridge[25] used the same procedure, with the substitution of an alkaline hypobromite treatment for the sulfuric acid hydrolysis, and they obtained results illustrating the effect of the mercerizing temperature, and of the concentration of the mercerizing solution (Figs. 55 and 56).

From a thermodynamic point of view both the change in crystal structure and the increase in amorphous material during the mercerization should result in a difference in energy content between native and mercerized cellulose. Several attempts have been made to determine this energy

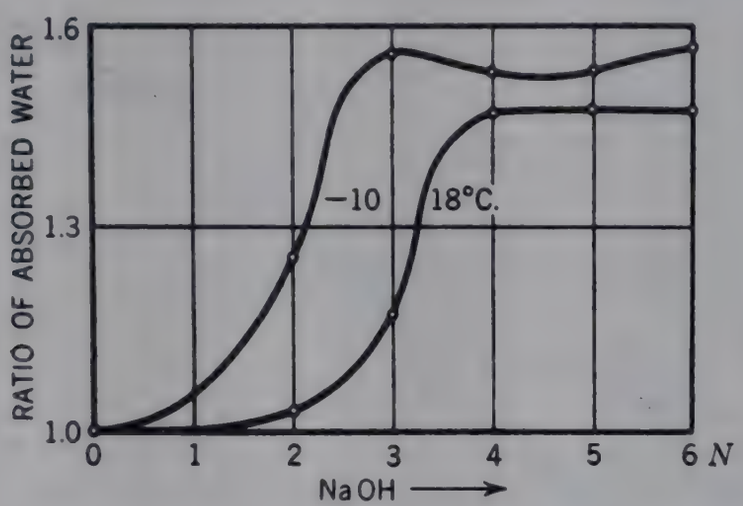

FIG. 56.—RATIO OF THE AMOUNT OF WATER ABSORBED BY COTTON WHICH WAS TREATED WITH NaOH SOLUTIONS OF VARIOUS CONCENTRATIONS AT 18°C. AND AT −10°C. TO THAT OF THE UNTREATED COTTON (BIRTWELL, CLIBBENS, GEAKE, AND RIDGE[25])

difference. Measurement of the heats of combustion revealed no difference. More successful, however, were the studies of Okamura[26] and of Morrison, Campbell, and Maass[27] based on the determination of the heat of reaction of cellulose with sodium hydroxide. At the mercerizing concentrations of alkali, obviously, both modifications of cellulose yield the same product and the difference in the heat of reaction therefore gives the difference in the energy content. Okamura used ramie fibers (Fig. 57). With zero concentration of sodium hydroxide, *i. e.*, with pure water, the mercerized form yielded the higher energy of wetting, a consequence of the larger "internal surface." There was very little rise in heat evolution for native ramie up to an alkali concentration of 5%, but above that concen-

[26] I. Okamura, *Naturwissenschaften*, **21**, 393 (1933).

[27] J. L. Morrison, W. B. Campbell, and O. Maass, *Can. J. Research*, **18B**, 168 (1940).

tration it was quite large. The heat of wetting of mercerized cellulose, on the other hand, rose rapidly with increase in alkali concentration up to 10% and then remained fairly constant up to 18%. Above 20% the difference between the heats of wetting of the native and the mercerized ramies was constant at a value even smaller than the difference between the heats of wetting in pure water. This constant difference of 1.5 cal. for each g. is, therefore, equal to the difference in energy content of the native and mercerized fibers, with the mercerized fibers having the higher energy content.

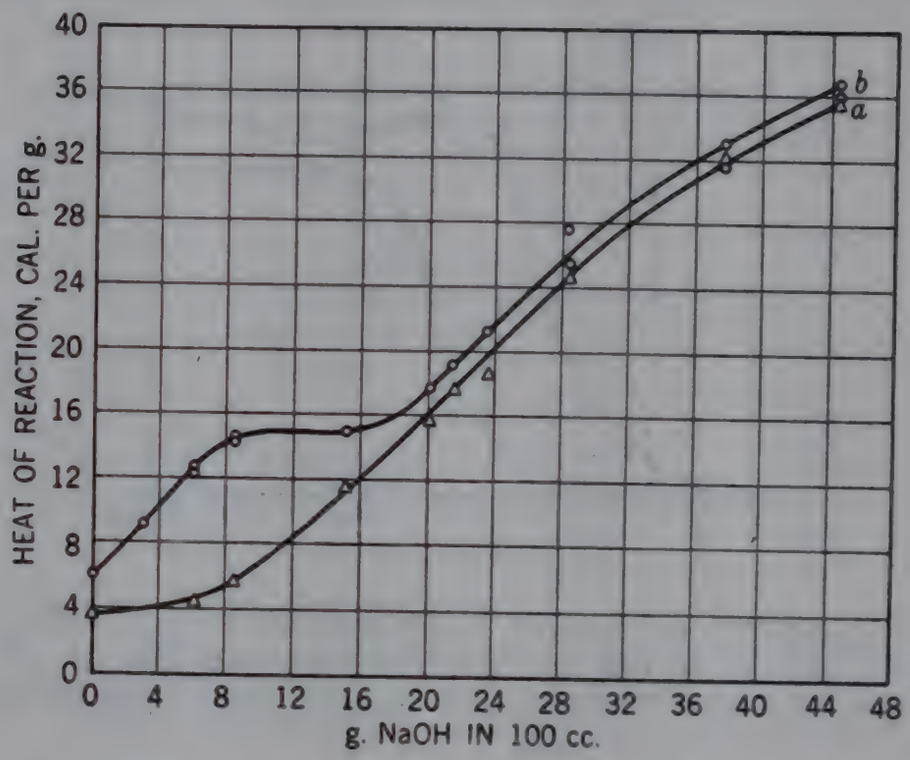

FIG. 57.—HEAT OF REACTION OF (a) NATIVE AND (b) MERCERIZED RAMIE WITH NaOH (OKAMURA[26]).

Morrison, Campbell, and Maass[27] obtained analogous results with bleached cotton, except that the energy differences were three times as large (Fig. 58). However, the absolute values of the heat evolved were also three times those for ramie, so that the ratios of the energy differences to the absolute values were practically unchanged. For bleached cotton, the energy content of the mercerized fibers was 6.6 cal. per g. higher than that of the native fibers.

Effects of the Change in Orientation of the Crystallites. If mercerization is carried out without tension, the cotton fibers shrink. Under identical conditions the extent of shrinkage depends on the tension applied. The x-ray diagram proves that by mercerization without tension the orientation of the

cellulose crystallites decreases. With careful application of tension, the degree of orientation of native cellulose can be retained or even increased. Obviously, the shrinkage of the fiber is caused by the disorientation of the cellulose crystallites which in the native fiber are preferably aligned with their major axis nearly parallel to the fiber axis (flax, ramie) or at a steep angle to the latter (cotton).

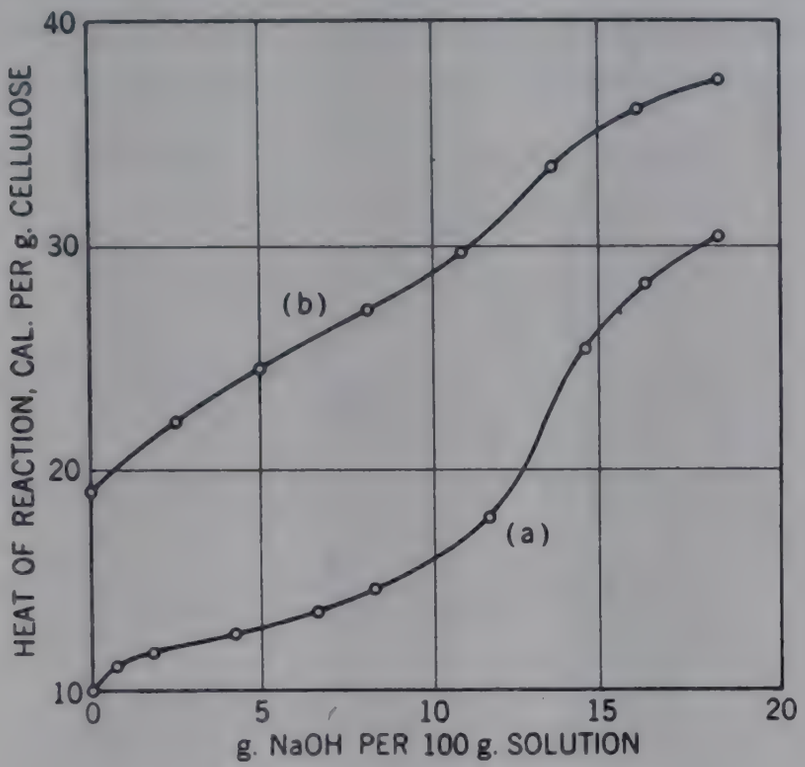

FIG. 58.—HEAT OF REACTION OF (a) NATIVE AND (b) MERCERIZED COTTON WITH NaOH (MORRISON, CAMPBELL, AND MAASS[27]).

The extent of shrinkage under identical conditions of tension varies with other factors similar to those affecting swelling: type of fiber, fiber surface characteristics, and alkali concentration.

The effect of the first factor mentioned was shown by the work of Nodder and Kinkead,[28] which showed that ramie and flax fibers contract to an even greater extent than cotton on mercerization. The smaller shrinkage of cotton is partly explained by the fact that the fibers, which are highly twisted in the native state, untwist in the alkaline solution. The removal of convolutions has itself a lengthening effect on the fibers, and the observed change in length is the resultant of this effect and of the contraction. Up to a sodium hydroxide concentration of about 8%, the effect of the

[28] C. R. Nodder and R. W. Kinkead, *J. Textile Inst.*, **14**, T133 (1923).

untwisting overbalances the contraction, and a lengthening of the fiber is observed.

Native, scoured, and rubbed fibers all show differences in the amount of shrinkage which they undergo on mercerization. Rubbed fibers show shrinkage even greater than that shown by scoured cotton (Fig. 59).

The effect of alkali concentration on shrinkage is similar to its effect on swelling when sodium hydroxide is used, but if other alkali hydroxides are included in the investigation, no general correlation between the shrinkage and the swelling can be established. Collins[29] carried out such experiments

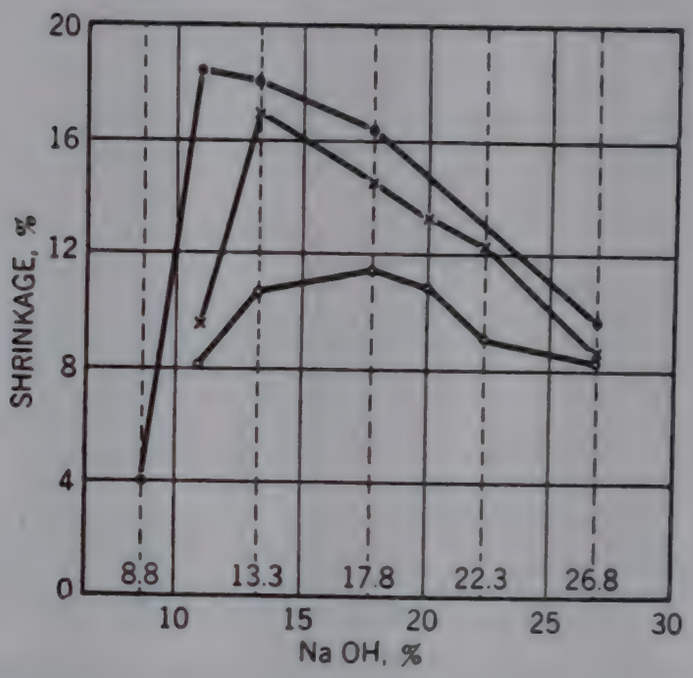

FIG. 59.—LONGITUDINAL SHRINKAGE OF COTTON FIBERS IN NaOH SOLUTIONS (CALVERT[8]).

Lower curve: raw hairs.
Middle curve: scoured hairs.
Upper curve: rubbed hairs.

with five different alkali hydroxides. His results are presented in Figure 60. The curves connect points found with increasing concentration of the hydroxides, the highest values of which are 48% NaOH, 52% KOH, 11% LiOH, 65% RbOH, and 80% CsOH. In these experiments the same fiber was exposed to alkali hydroxide solutions of increasing concentration and no maximum was observed in the shrinkage. Striking differences between the effects of the alkalies are observed when the changes in length, which correspond to an increase of, for example, 25% in the diameter of the fiber, are compared.

[29] G. E. Collins, *J. Textile Inst.*, **16**, T123 (1925).

The effect of the surface layer of the fiber on the shrinkage is somewhat similar to that of the tension. This is demonstrated by the fact that, for instance, the shrinkage diagram of scoured cotton can be modified to be similar to that of raw cotton by applying tension during the alkali treatment (Fig. 61). If the tension is applied before the treatment with caustic, much less tension is required to obtain the same lowering of shrinkage

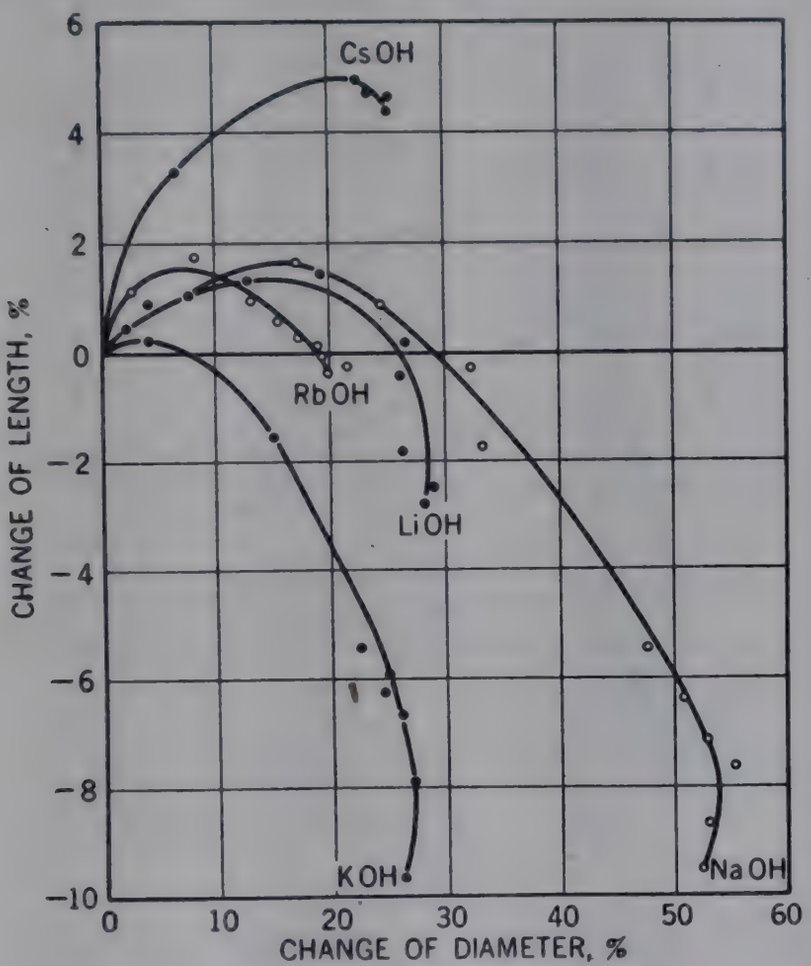

FIG. 60.—RELATIONSHIP BETWEEN THE CHANGE OF LENGTH AND THE CHANGE OF DIAMETER OF THE FIBERS IN ALKALI HYDROXIDE SOLUTIONS (COLLINS[29]).

(Fig. 62). Obviously, a state of equilibrium is not completely attained. Measurements of the absolute magnitude of the tension which is necessary to prevent shrinkage of fibers were carried out by Herzog,[30] who found that 3.8, 3.0, and 2.2 kg./mm.^{2} prevented shrinkage when KOH, NaOH, and LiOH of 40%, 25%, and 10% concentration, respectively, were used.

The changes in orientation are reflected in the changes in the refractive

[30] R. O. Herzog, *Kolloid-Z.*, **39**, 98 (1926).

indices of fibers during mercerization. Preston[31] observed that both the transverse refractive index n_α and the axial refractive index n_γ are lowered by mercerization without tension (Table 6). He calculated from the changes in index an average angle of inclination of the crystallites to the axis of the fiber and, from the angle of inclination, the contraction which the fiber underwent during the alkali treatment. Incidentally, the fact that n_α dropped on mercerization instead of rising to approach n_γ demon-

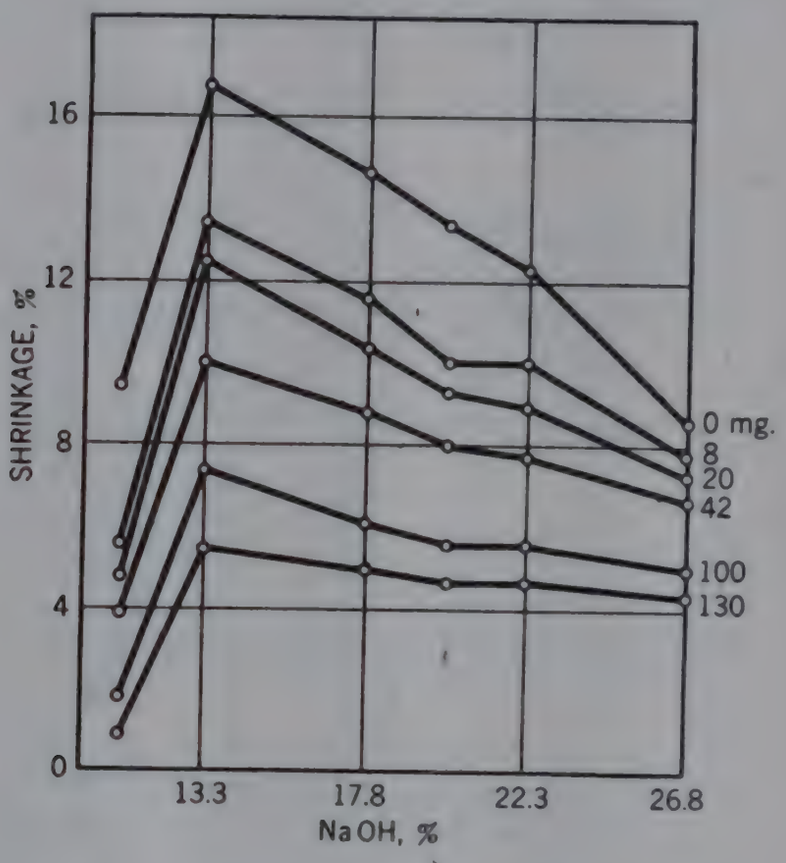

FIG. 61.—LONGITUDINAL SHRINKAGE OF SCOURED COTTON FIBERS MEASURED UNDER VARIOUS TENSIONS AFTER FREE SHRINKAGE WAS ALLOWED (CALVERT[8]).

strated that the single crystallite of mercerized cellulose has a lower refractive index than has the single crystallite of native cotton.

The most important fiber properties which are affected by the orientation of the crystallites are breaking strength and extensibility. The extensibility of a highly oriented fiber is very small, but its breaking strength is high. In fact, Schubert[32] reported that single fibers mercerized under tension had higher breaking strengths than did native fibers (Fig. 63).

[31] J. M. Preston, *Trans. Faraday Soc.*, 29, 65 (1933).
[32] C. Schubert, Dissertation, Dresden, 1932.

This effect is probably due to the production of a more uniform fiber cross section by the swelling process. The claim has repeatedly been made that

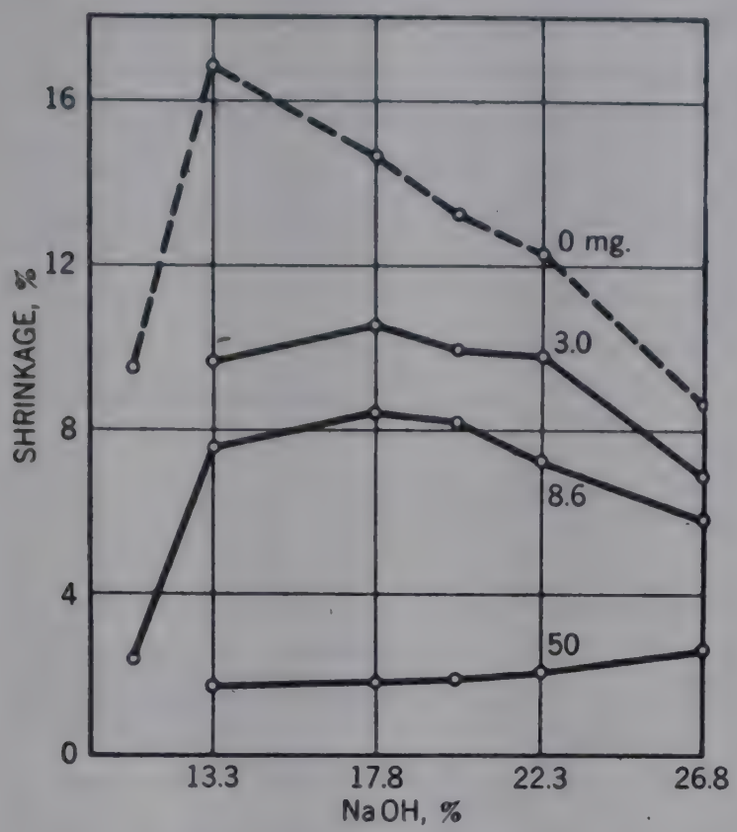

FIG. 62.—LONGITUDINAL SHRINKAGE OF SCOURED COTTON FIBERS WHEN TREATED UNDER VARIOUS TENSIONS WITH NaOH SOLUTIONS (CALVERT[8]).

TABLE 6

CHANGES IN THE REFRACTIVE INDICES OF CELLULOSE FIBERS CAUSED BY MERCERIZING (PRESTON[31])

Fiber	n_γ	n_α	$n_\gamma - n_\alpha$
Ramie and flax, native	1.596	1.528	0.068
Flax, mercerized under tension	1.571	1.517	0.054
Flax, mercerized without tension	1.556	1.518	0.038
Cotton, native	1.578	1.532	0.046
Cotton, mercerized under tension	1.586	1.522	0.044
Cotton, mercerized without tension	1.554	1.524	0.030
Lilienfeld rayon	1.559	1.515	0.044
Lilienfeld rayon, mercerized without tension	1.550	1.515	0.035

mercerizing increases the mechanical strength of fabrics and yarns also. The quantitative data on this subject are, however, contradictory.

Changes Produced in the Microscopic Structure of the Fibers. For an understanding of the increased luster (technically the most important change produced by mercerization) a study of the changes produced in the microscopic structure of the fiber is required. Immediately before the ripe boll bursts open and exposes its flocks of cotton to the atmosphere, the fibers are tubular, with the hollow center (the "lumen") occupying a considerable portion of the cross section. No convolutions or twists are present, and the cross sections approach very closely to an elliptical or even

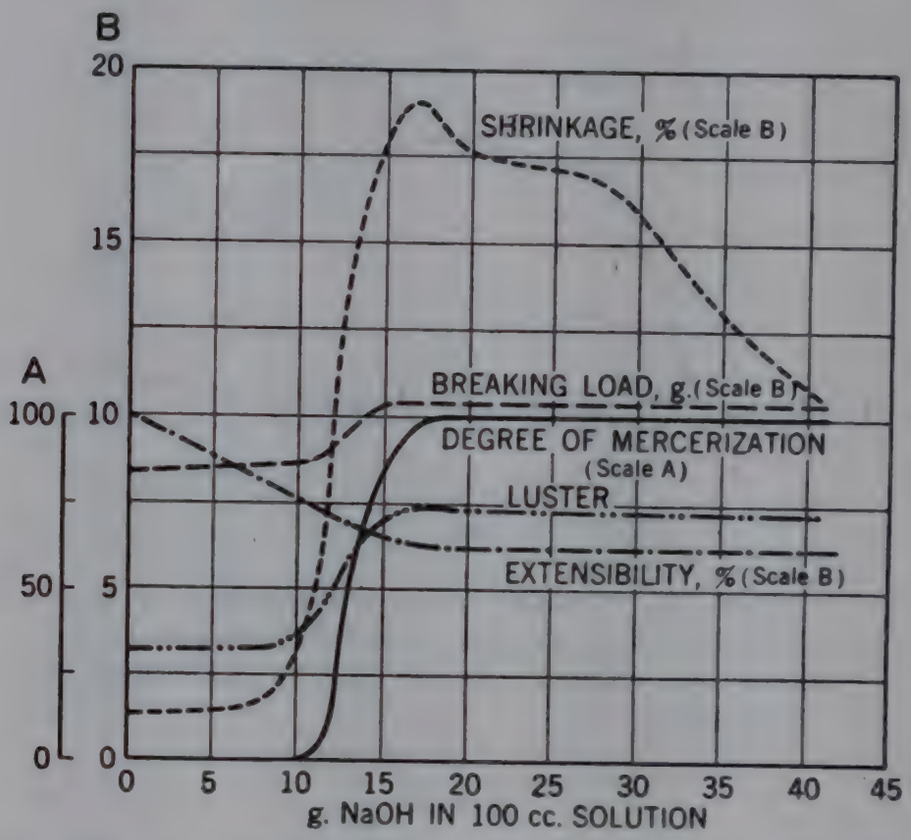

FIG. 63.—DEPENDENCE OF THE PROPERTIES OF COTTON FIBERS ON THE CONCENTRATION OF THE MERCERIZING SOLUTION (SCHUBERT[32]).

circular form. On exposure to the air, the fiber dries out quickly and collapses to form a flat, convoluted ribbon. Commercial cotton hair is in this form.

When the cotton hair is brought into a mercerizing solution, it begins to swell at once. In a few seconds it becomes elliptical, and, on further swelling, the cross section becomes almost circular. The diameter of this section is at least 25 to 30% greater than the width of the collapsed fiber.[33] These stages of the swelling are shown diagrammatically in Figure 64. During

[33] M. A. Calvert and F. Summers, *J. Textile Inst.*, 16, T233 (1925).

the mercerizing process, the cellulose of the wall swells inwardly. After the alkali treatment and during the washing and drying, the cross section shrinks. During this shrinkage, the hair retains the same circular form, but the shrinkage proceeds uniformly toward the axis and the lumen does not recover its original size.

There are some features of this process which are not fully understood. There was an opinion that the original circular form of the undried, ripe cotton hair was restored by mercerization. However, the lumen of the mercerized hair is filled with cellulose to an extent which is never encountered at any stage of development of the native fiber. There is obviously

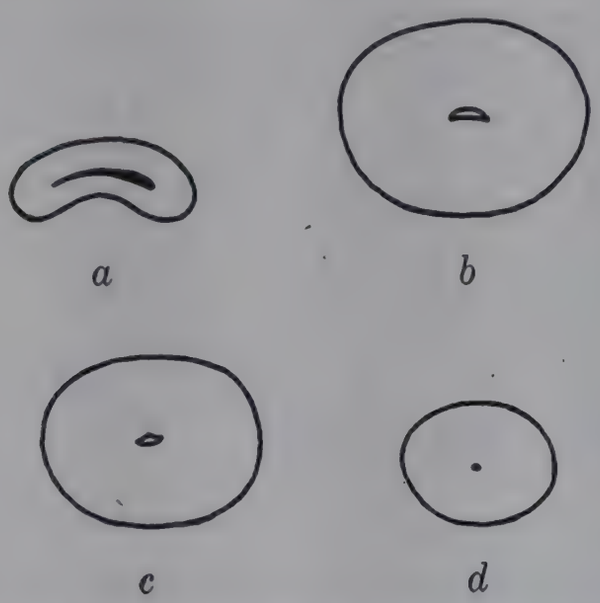

FIG. 64.—CHANGES OF THE FORM OF THE CROSS SECTION OF COTTON FIBERS DURING MERCERIZING (CALVERT AND SUMMERS[33]).

Key: (*a*) Fully collapsed hair.
(*b*) Same, swollen in 18% NaOH solution.
(*c*) Same, washed with water.
(*d*) Same, washed and dried.

some kind of organization in the native cotton fiber, possibly between the fibrils, which provokes its collapse on exposure to air. On the other hand, it seems necessary to assume that the outer wall of the fiber functions somewhat as a skin which exerts a mechanical restraint on the mercerization process and which is responsible for the cylindrical form attained during the mercerizing. By the strong swelling, the arrangement which was responsible for the collapse of the native hair is broken up, and the cylindrical form is retained upon subsequent drying.

The surface of the hair which has been treated in mercerizing solution

without tension is smoother than that of the native fiber and the convolutions have disappeared, but, if the mercerizing is carried out under tension, the lumen is even more constricted, the transverse section is perfectly cylindrical, and the surface is perfectly smooth. The numerous folds and indentations are completely eliminated. Obviously, drying causes a certain constriction of the skin which results in folds and creases of the surface, provided no tension is applied. By what mechanism the application of the tension during the swelling, *i. e.*, the stretching of the skin in the direction of the fiber axis at the expense of the perimeter, prevents the folding during the subsequent drying operation, is not clear. Possibly

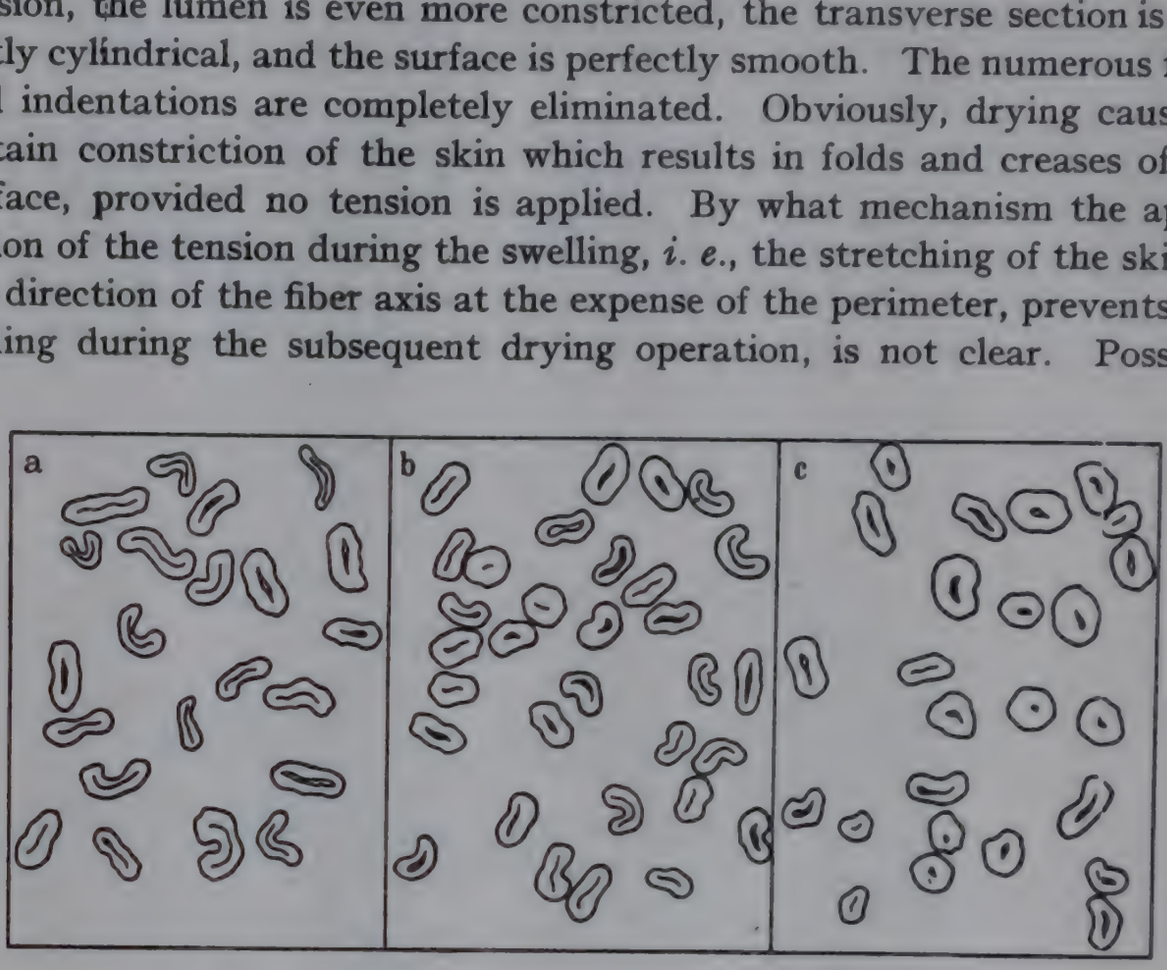

FIG. 65.—CROSS SECTIONS OF COTTON HAIRS (ADDERLEY[84]).

Key: (a) Native cotton hairs with low luster with average ratio of length of major axis to that of minor axis equal to 2.95.
(b) Native cotton hairs with high luster with average axis ratio of 2.00.
(c) Mercerized cotton hairs with average axis ratio of 1.60.

peculiarities of the organization of the primary wall have a decisive role here.

Through quantitative measurements on single fibers, Adderley[84] demonstrated that the luster of cotton increases as the cross section of the hairs approaches a circular form. The correlation is a very good one, regardless of whether the cotton is mercerized or native (Figs. 65 and 66). The luster of flax and ramie, which is considerable even in the native state, is not increased by the mercerizing process. It seems, therefore, that the microscopic fiber structure is the determining factor in the amount of luster possessed by a fiber.

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[84] A. Adderley, *J. Textile Inst.*, **15**, T195 (1924).

2. Theory of Mercerization

The change in dimensions of the cellulosic fiber in the process of mercerization without tension is the resultant of two components: swelling, which occurs mainly in the transverse direction, and shrinking, which occurs in the direction of the fiber axis. The first change is reversible with washing and drying, while the second is not. That the swelling is more pronounced in the transverse direction is easily explained by the assumption that the

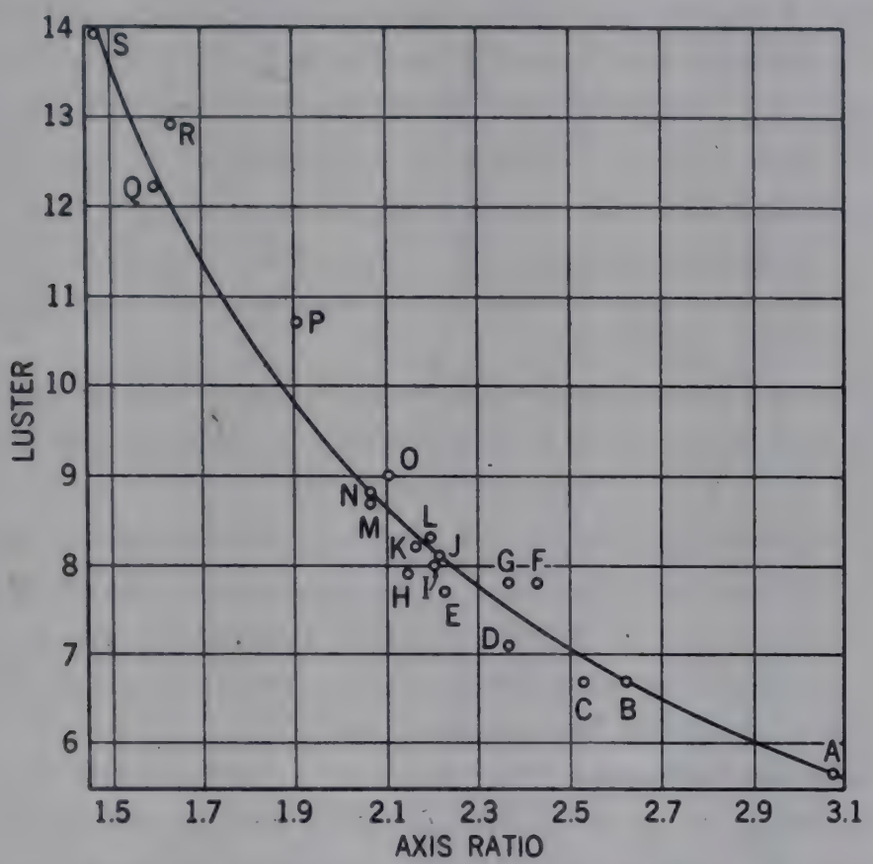

FIG. 66.—LUSTER NUMBER OF COTTON FIBERS AS A FUNCTION OF THE RATIO OF THE LENGTH OF THE MAJOR AXIS OF THE CROSS SECTION TO THAT OF THE MINOR AXIS (ADDERLEY[34]).

A–P: Native cotton.
Q–S: Mercerized cotton.

take-up of water occurs mostly in the transverse direction to the cellulose chains and crystallites and that the latter are preferably oriented parallel to the fiber axis. Nevertheless, the fact of contraction in length requires an explanation; because of the importance of shrinkage and tension in the mercerization process, this explanation occupies the foremost place in the theory of the mercerization.

The present knowledge of the mechanical properties of high-polymeric substances permits a derivation of such a theory. According to the ideas of

Bungenberg de Jong,[35] Hermans and de Leeuw,[36] and Kratky,[37] the crystalline regions of the cellulose fiber are bound in a mesh of amorphous cellulosic material. In the native fiber the amorphous material is in the extended state, *i. e.*, the cellulose molecules have more or less the form of straight rods, probably as a consequence of the natural growth process. According to the theory of Meyer, von Susich, and Valko,[38] the extended chain molecules have a tendency to regain a statistically more probable configuration: that corresponding to a coil or tangle of thread. This tendency is the basis of the rubber-like elasticity of all elastomers. The elaboration of this idea in a quantitative way was furnished by Mark and his coworkers[39] and independently by Kuhn.[40] The high viscosity of the cellulosic material does not allow a contraction of the chains. The swelling in sodium hydroxide solution diminishes the friction between the chains thus allowing the contraction. Since the crystallites are suspended in the mesh of the extended chains, the contraction of these chains causes a disorientation of the crystallites.

According to the above theory, native cellulose can be compared with rubber which has been cooled under tension and, because of the high viscosity, does not contract after release of the tension until it is brought again to a certain temperature. Similar phenomena are shown by other high-polymeric substances, such as: collagen, which, when it is dry, shrinks at 90–120°C., but when it is wet, shrinks even at 60–80°C.[39]; and silk, which shrinks extensively on exposure to the swelling action of formic acid to give a product of rubber-like elasticity.

The fact that the shrinkage phenomenon of native cellulose fibers is not due to some peculiarity of the native fibrillar structure is demonstrated by the observation that cellophane[41] and cuprammonium rayon[42] display a completely analogous shrinkage in caustic soda solution. These materials are fixed in the extended state by the coagulation under tension during the spinning process. Bungenberg de Jong subjected cellulose xanthate in the plastic state to a stress and fixed it in the extended state by treatment with acid. He found that cellulose so obtained undergoes even in water a longitudinal contraction with a simultaneous increase in diameter.

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[35] H. G. Bungenberg de Jong, *Z. physik. Chem.*, **130**, 205 (1927).
[36] P. H. Hermans and A. J. de Leeuw, *Kolloid-Z.*, **81**, 300 (1937).
[37] O. Kratky, *Kolloid-Z.*, **70**, 14 (1935).
[38] K. H. Meyer, G. von Susich, and E. Valko, *Kolloid-Z.*, **59**, 208 (1932).
[39] E. Guth and H. Mark, *Monatsh.*, **65**, 93 (1934).
[40] W. Kuhn, *Kolloid-Z.*, **68**, 2 (1934); **76**, 258 (1936); **87**, 3 (1939).
[41] G. van Iterson, Jr., *Chem. Weekblad*, **30**, 2 (1933).
[42] G. Saito, *Kolloid-Beihefte*, **49**, 365 (1939).

3. Optimum Conditions for Mercerization

A determination of the optimum conditions for mercerization is of interest from the commercial point of view. The properties of the mercerized fibers which are important are luster, breaking strength, and extensibility, while the variables which may change these properties are the time of treatment, the temperature of treatment, the concentration of alkali, the tension, and the previous treatment of the fibers.

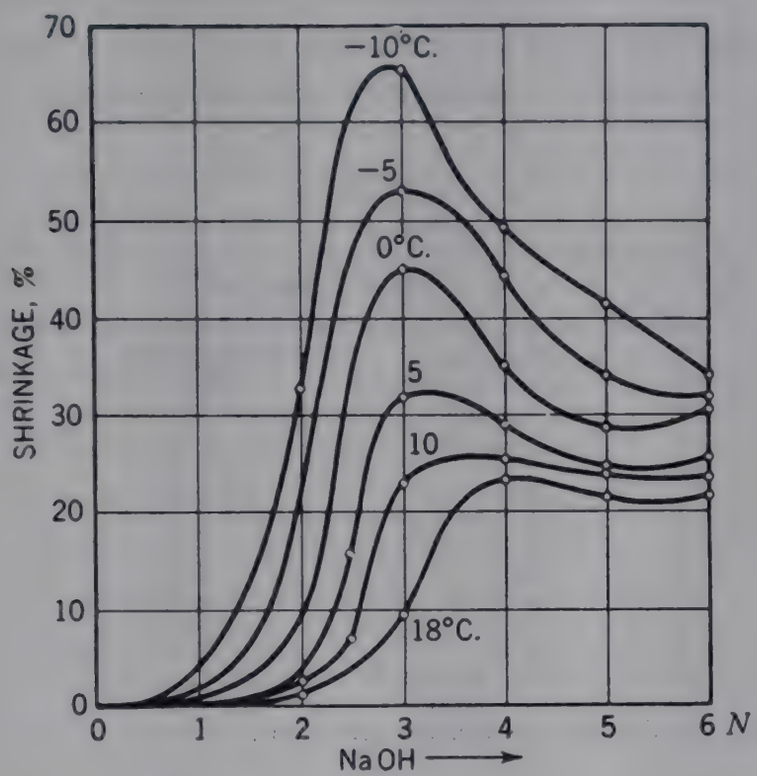

FIG. 67.—SHRINKAGE OF COTTON YARN SUFFERED BY TREATMENT WITH NaOH SOLUTIONS OF VARIOUS CONCENTRATIONS AT VARIOUS TEMPERATURES (BIRTWELL, CLIBBENS, GEAKE, AND RIDGE[25]).

Schubert[32] has investigated the effect of the sodium hydroxide concentration. The fibers were allowed to shrink and then were stretched to their original length before washing out the caustic soda. The shrinkage obtained with the caustic soda before stretching was noted. The degree of mercerization of the finished fiber was measured by the extent of the change in the x-ray diagram. The results (Fig. 63) show that the breaking strength, as well as the luster, reached its highest value at about 16% NaOH and an increase in the concentration of the alkali brought no further change in these properties. The x-ray diagram showed that the

degree of mercerization was 100% at about 18% NaOH. The shrinkage has an optimum value at about 17% NaOH. The extensibility decreases with increasing concentration and the lower limit is reached at 16% NaOH, probably as a result of complete untwisting of the fiber.

A systematic investigation of the effect of temperature and concentration of the mercerizing solution on the properties of cotton yarn was carried out by Edelstein.[43] The temperatures were 15°C., 32°C., and 43°C., and the NaOH concentrations, 13%, 15.5%, 22.5%, and 29%. It was found, in agreement with the results of Birtwell, Clibbens, Geake, and Ridge[25] (Fig. 67), that the lower the temperature of the particular caustic solution, the greater was the tension necessary to prevent the yarn from shrinking in

TABLE 7

EFFECT OF STRETCHING DURING MERCERIZING ON THE PROPERTIES OF EGYPTIAN COTTON FIBERS* (SCHUBERT[32])

Stretched, mm.	Breaking load, g.	Extension at break, %	Luster number
0.00	9.8	16.3	4.3
1.00	9.8	11.1	5.7
1.90	10.2	9.4	6.5
2.65	10.2	6.5	7.8
3.00	10.4	5.8	7.7
3.45	10.4	5.3	7.3

* Original length 14.80 mm.; shrinkage 2.62 mm.

the solution and the greater was the dye affinity, the barium absorption ratio, and the tensile strength of the mercerized yarn. However, the effect of temperature on the mercerization was slight when caustic solutions of high concentration were used. With caustic solutions at lower concentrations, the maximum luster was reached at the lowest temperature, but, with a caustic solution of 50 to 65° Twaddell (23–30%), it was reached at a temperature of 32°C.

The effect of tension when applied after shrinkage was allowed is shown in Table 7. The optimum luster was reached when the original length was restored, but the absolute strength, per unit of diameter of fiber, increased slightly on further increase in the amount of stretching. When this absolute strength is calculated, the decrease in diameter of the fiber by the stretching is to be taken into account.

[43] S. M. Edelstein, *Am. Dyestuff Reptr.*, 25, P458, P724 (1936); 26, P423 (1937).

Edelstein[43] found that the greater the tension applied to the yarn in a particular caustic solution, the greater was the luster and the less was the affinity for dyes of the finished material. This holds even if the tension is much higher than that which is just necessary to prevent shrinkage. These findings do not disagree with the results of Schubert (Table 7) on single fibers, if it is taken into account that a tension which may be sufficient to prevent shrinkage of the yarn or fabric as a whole is not necessarily sufficient to prevent the shrinkage of the single fiber by slipping.

In commercial practice the fibers are generally not allowed to remain in contact with the mercerizing solution for more than a minute. It is therefore necessary to obtain a complete penetration of the fabric or yarn in this short time. This is generally achieved by using scoured (alkali-boiled) cotton. If the mercerization is carried out with raw cotton, a wetting agent must be added to the bath. These agents are surface-active substances which are stable even at the high sodium hydroxide concentration used and which lower the interface tension against the surface impurities of the fiber. The most widely used agents are higher homologs of phenol.

E. THE DISTRIBUTION OF SUBMICROSCOPIC METAL CRYSTALS IN FIBERS

CHARLES W. HOCK AND H. MARK

In order to obtain information on the supermolecular structure of cellulose, it is necessary to determine the size and shape of the crystallites[1] and of the interstices between them. The average size and shape of the micelles have been estimated by the use of x-rays, and are described in Section A of this chapter.[4–9] In well-oriented native fibers, such as flax, hemp, or ramie, the crystallites of cellulose have, on the average, a length of more than 600 Å., while their average width is between 50 and 100 Å.

The investigation of the intermicellar system of pores and capillaries can be carried out microscopically as long as the investigations are confined to the large gross structure of the system. If, however, the interstices are of order of magnitudes below 1 micron, it is necessary to apply other methods. One which has proved to be quite informative is the use of double refraction, which also is described elsewhere (see Section C of this chapter). The other, which perhaps has contributed most to our present knowledge of imperfections and cavities in cellulose fibers, is based on the distribution of

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[1] The word *micelle* was first proposed by Nägeli[2] on the basis of microscopic observations with polarized light. At that time it was not known that these particles were crystalline. This was shown later by Herzog[3] and by Scherrer[4] who introduced the term *crystallite*. In the present paper the two terms are used interchangeably.

[2] C. Nägeli, *Die Micellarlehre*. Ostwald's *Klassiker* No. 227. Leipzig, 1928; *Stärkekörner*. F. Schulthub, Zürich, 1858; *Theorie der Gärung*. R. Oldenbourg, München, 1879.

[3] R. O. Herzog, *J. Phys. Chem.*, **30**, 459 (1926).

[4] P. Scherrer in R. Zsigmondy's *Kolloidchemie*. 3rd ed., O. Spamer, Leipzig, 1920, p. 387.

[5] M. von Laue, *Z. Krist.*, **64**, 115 (1926).

[6] A. L. Patterson, *Z. Krist.*, **66**, 637 (1928).

[7] R. Brill, *Z. Krist.*, **63**, 388 (1928).

[8] R. Brill and H. Pelzer, *Z. Krist.*, **74**, 147 (1930).

[9] W. T. Astbury, *Trans. Faraday Soc.*, **29**, 193 (1932).

submicroscopic metal crystals in the fiber, and the subsequent investigation of these crystals with the ultramicroscope and with x-rays.[10–23]

Before describing the developments in this field, it may be pointed out that a knowledge of the pores and capillaries in cellulose fibers, particularly in synthetic ones, is essential to the proper understanding of their mechanical properties, such as tenacity, elongation, and resilience. (See Chapter IX.)

1. Methods of Depositing Metal Crystals in Fibers

Berkman, Böhm, and Zocher[10] were the first to attempt an investigation of cellulose fibers by distributing small crystals in the spaces between the cellulose crystallites. They soaked the fibers in dilute solutions of heavy-metal salts and dyestuffs and precipitated the crystals in an appropriate way. A comparatively small amount of crystallized substance was distributed in the sample, and the fibers thus prepared were investigated with x-rays. The purpose was to find out whether or not the crystals deposited in the pores and capillaries of the cellulose structure would be oriented. The diagrams showed that they were unoriented, and this was taken as an indication that their shape was not elongated, but isodiametric. No further attempt was made to study these diagrams more elaborately at this time.

Later, this method was taken up by Frey-Wyssling,[12,18] who improved it very considerably, and succeeded in obtaining very interesting results by a combined use of the ultramicroscope and the polarizing microscope. In collaboration with Kratky[16] and Schossberger,[19] he extended his studies

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[10] S. Berkman, J. Böhm, and H. Zocher, *Z. physik. Chem.*, **124,** 83 (1926).

[11] O. Gerngross, K. Hermann, and W. Abitz, *Z. physik. Chem.*, **B10,** 371 (1930).

[12] A. Frey-Wyssling, *Protoplasma*, **25,** 261 (1936); **26,** 45 (1936); **27,** 372, 563 (1937).

[13] E. Guth and S. Rogowin, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse*, Abt. IIa, **145,** 531 (1936).

[14] F. Breuer, O. Kratky, and G. Saito, *Kolloid-Z.*, **80,** 139 (1937).

[15] P. H. Hermans, *Kolloid-Z.*, **81,** 143 (1937).

[16] O. Kratky and H. Mark, *Z. physik. Chem.*, **B36,** 129 (1937).

[17] E. Sauter, *Z. physik. Chem.*, **B35,** 129 (1937).

[18] A. Frey-Wyssling, *Kolloid-Z.*, **85,** 148 (1938).

[19] O. Kratky and F. Schossberger, *Z. physik. Chem.*, **B39,** 145 (1938).

[20] H. Mark, *J. Phys. Chem.*, **44,** 764 (1940); *Papier-Fabr.*, **36,** Tech.-wiss. Tl., 57 (1938).

[21] R. Hosemann, *Z. Elektrochem.*, **46,** 535 (1940).

[22] H. Mark, *High Polymers*, Vol. 2, *Physical Chemistry of High Polymeric Systems*. Interscience, New York, 1940.

[23] K. H. Meyer, *High Polymers*, Vol. 4, *Natural and Synthetic High Polymers*. Interscience, New York, 1942.

to the use of x-rays, and reached certain general conclusions about the supermolecular structure of native fibers which seem to be of considerable interest. The experimental procedure is to treat the specimens with dilute solutions (1 to 2% by weight) of heavy-metal salts, such as silver nitrate, gold chloride, platinum chloride, and mercury nitrate, at room temperature for about one to two hours. The treatment is carried out in slightly acidic solution in the dark, in order to prevent premature precipitation of the metal. After the fibers have been thoroughly soaked with the solution, they are taken out, rinsed with distilled water, and dried with blotting paper. Finally, they are exposed to an appropriate reducing agent. With some salts, such as gold chloride, exposure to daylight is sufficient for reduction and for deposition of crystals. In other cases, such as with silver or silver amalgam, it is necessary to apply reducing agents such as formaldehyde. With all materials, it is essential to carry out the imbibition and the reduction very slowly and gently.

2. Methods of Studying Metal Deposits in Fibers

The samples thus prepared have been studied by the following different methods: (a) x-rays, (b) double refraction, and (c) ultramicroscope.

(*a*) *X-rays*

Frey-Wyssling,[12,18] Kratky,[16] and Schossberger[19] have investigated the x-ray intensity scattered by fibers containing metal deposits, and have compared it with the intensity scattered by the same fibers without metals. The results indicated that the deposition of a very small amount of gold (about 1% by weight or 0.1% by volume) in native ramie fibers increases the intensity of the cellulose interference spots by about 100%, produces an increase of about 200% in the intensity scattered under small angles (30 minutes or less), and gives the interference lines characteristic for the diagram of gold or platinum. Analysis of this powder diagram proved that the gold is present in its normal face-centered modification with the lattice constant of $a = 4.070$ Å. The width of the interference lines shows that the crystals are isodiametric and have an average diameter of about 100 Å.

The intensity scattered under small angles was interpreted as being indicative of the presence of extremely thin, heavy-metal lamellae arranged between the oriented crystallites of cellulose and presumably distributed in the amorphous areas of the sample. These thin, heavy-metal sheets produce a super-lattice structure with an average grating constant of about 70 Å. This distance indicates the thickness of the cellulose crystallites and

is in reasonable agreement with the values derived from the width of the cellulose interference spots as indicated on pp. 215*ff*.

No completely satisfactory explanation has yet been advanced for the increase in the intensity of the cellulose interference spots obtained by depositing heavy metals in the interstices of the fiber. Kratky and Schossberger[19] suggest that the crystals of the metal induce a certain amount of cellulose to undergo additional crystallization, and hence increase the intensity of the interference spots. This is an explanation which may give interesting indications as to the nature of the transition of amorphous cellulose to crystallized cellulose. It is supported by the fact that, upon removal of the heavy metal, the additional intensity does not entirely disappear. This would mean that some of the chains which have been induced to crystallize remain in the crystallized state, while others (which have not been definitely attached to the crystals) return to the amorphous part of the material.

It may be added that Hosemann[21] has recently made an interesting attempt to draw far-reaching conclusions from the intensity scattered under small angles. Unfortunately, however, as Meyer[24] points out, it seems that the experimental technique applied by Hosemann may not have been adequate.

(*b*) *Double Refraction*

Frey-Wyssling[12,18] has very thoroughly studied the double refraction of native cellulose fibers containing small metal crystals, and has found a distinct increase in birefringence. By using the method of embedding the fibers in liquids of different refractive indices, he was able to interpret this additional birefringence in the following way: About 0.1% of the volume of the fiber is occupied by metal particles having the shape of a rod or spindle, with an average length of about 2500 Å. and a maximum diameter of around 400 Å. These spindles are irregularly distributed throughout the specimen, but their long axes are all parallel to the fiber axis. Their average mutual distance is of the order of magnitude of 3000 Å.

(*c*) *Ultramicroscope*

Corroborative evidence for the existence of such particles as those postulated by the results of double refraction studies was also obtained by Frey-Wyssling[18] when he succeeded in detecting them by direct investiga-

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[24] K. H. Meyer, *Z. Elektrochem.*, **47**, 363 (1941).

tion in the ultramicroscope. Thus, investigations by methods (b) and (c) led to concordant results.

A comparison of these results with those of the x-ray investigation makes it clear that the particles found by x-rays (having a diameter of around 100 Å.) are much smaller than the spindle-shaped particles observed by optical methods. This, however, is a case which is well known in colloid physics. The x-rays measure the primary particles or the mosaic crystallites, while the optical methods measure the secondary particles or the aggregate built up by the mosaic crystallites. It is, therefore, reasonable to assume that the elongated particles as discovered by the optical methods are secondary particles built up from the cube-shaped crystallites indicated by the x-ray method.

3. Results

Attention is now directed to Figure 68 in which an attempt has been made to sketch the results of these investigations. The metal seems to appear in three states: (1) as extremely thin intermicellar lamellae; (2) as cube-shaped primary particles; and (3) as spindle-shaped secondary particles.

Figure 68A, which corresponds to a magnification of about 300,000 to one, shows part of a fiber having a diameter of about 1000 Å. and a length of about 1500 Å. The thin lines giving an irregular pattern throughout the fiber represent layers of heavy-metal lamellae deposited in the amorphous areas between the cellulose crystallites, having a thickness of only a few atoms. Their average distance coincides with the width of the micelle and is of the order of magnitude of 70 Å. These lamellae appear to form a matrix in which the cellulose micelles are embedded. The lower part of the right side of Figure 68A is occupied by an empty pore, which is assumed to be filled with metal crystals (primary particles) having an average diameter of about 100 Å. and aggregated to form a secondary particle which is about 400 Å. thick and 2500 Å. long.

Figure 68B shows the same situation with a magnification of about 100,000 to one. Again only a portion of the fiber, 3000 Å. thick and 5000 Å. long, is represented. The fine lamellar structure has now disappeared, and only the primary particles of the metal and the secondary particles built from them can be seen. The different distances characteristic of this arrangement are indicated in Figure 68B.

Finally, Figure 68C shows a still smaller magnification (12,000 to one), such as is obtainable in the ultramicroscope. The portion of the fiber under investigation is now 25,000 Å. thick and about 75,000 Å. (7.5 microns) long. All that can be seen now are the secondary particles and their geometrical

arrangement in the fiber, as indicated by the birefringence of such samples in mediums of different refractive indices.

It can be seen that the combined use of optical and x-ray methods allows quite far-reaching conclusions to be drawn about the structure of the intermicellar cavities in native fibers. Similar investigations of artificial materials

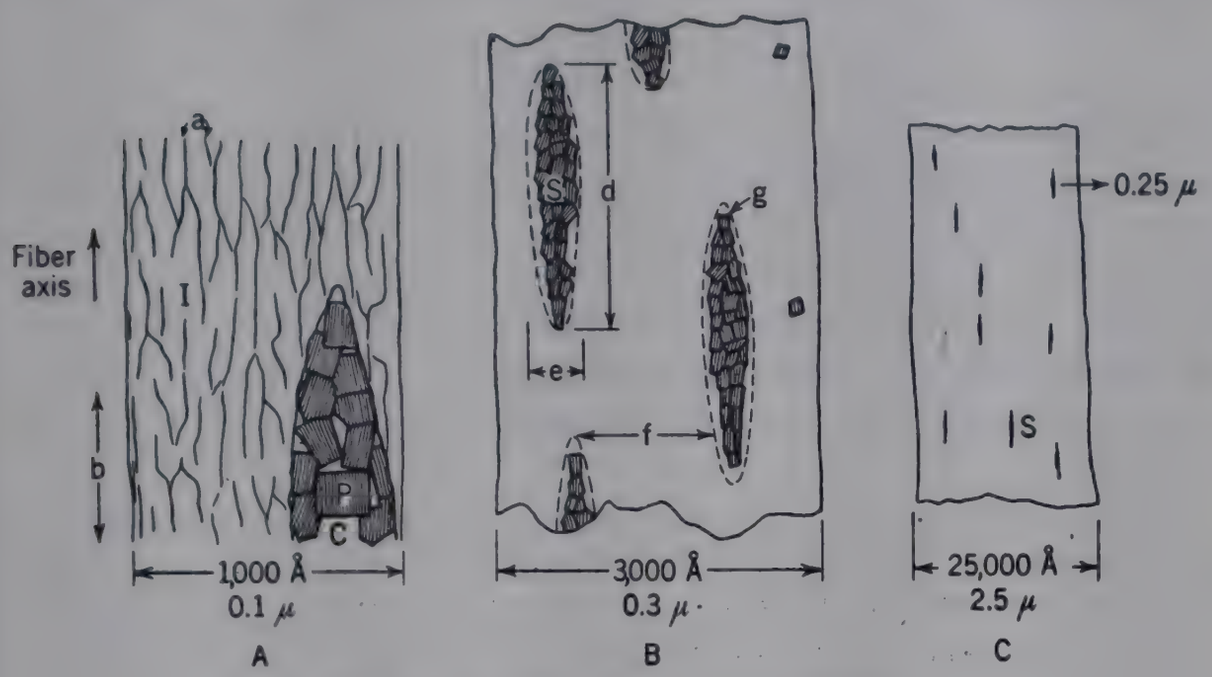

FIG. 68.—METAL DEPOSITS IN FIBERS.

P. Primary particles.
S. Secondary particles.
I. Intermicellar lamellae.

a. Average width of the cellulose crystallites; about 70 Å.

b. Average length of the cellulose crystallites; greater than 600 Å.

C. Empty pore, which can be filled with roughly cubical crystals (primary particles) to give a secondary particle.

d. Long axis of spindle-shaped secondary particles; about 2500 Å.

e. Short axis of spindle-shaped secondary particles; about 400 Å.

f. Average distance between secondary particles; about 3000 Å. (in the figure reduced to $^1/_2$).

g. Average size of cube-like primary particles; about 100 Å.

Magnification: A, × 300,000; B, × 100,000; C, × 12,000.

such as rayon or cellophane would presumably lead to interesting conclusions concerning the relation between the processes of spinning or casting and the internal structure of the specimens. Finally, it may be pointed out that the electron microscope should provide a new method of obtaining additional and more specific information as to the size, shape, and distribution of the metal deposits which cannot be obtained by the other methods hitherto used.

F. BEATING AND HYDRATION OF PAPER FIBERS

JAMES D'A. CLARK

When fibrous cellulose is pounded, ground, rubbed, or otherwise subjected to mechanical action in the presence of water, its behavior is changed in a manner which makes the process of considerable technical importance. The resulting product is said to be "beaten." Its outstanding characteristic lies in the ability of fibers so treated, and thereafter dried in contact with one another, to adhere strongly together. The beaten fiber mass also acquires a slimy feel and the property of holding water longer when allowed to drain.

The process as carried out technically is referred to as "beating." The fiber suspension ("stuff" or "stock") is said to be "beaten," "wet," "slow," or "hydrated." Before beating, the condition of the pulp is termed "unbeaten," and after only a mild beating treatment "free." "Wetness," "slowness," and "freeness" are derived words. These technical terms refer to the ease or difficulty with which the pulp, when squeezed in the hand or placed on a screen, either retains or parts with some of its associated water.

Beating is extremely important in its relation to the quality and the rate of production of paper. In fact, it has been said with much truth that paper is "made" in the beater. Furthermore, interest in the subject among paper technologists has been heightened by the fact that in the beating operation an enormous amount of power is consumed daily—from 200 to nearly 2000 kilowatt hours per ton of finished paper for certain specialties, although it is not often that a figure of 1000 is exceeded. Even so, with an annual production of over fifteen million tons of paper and board in the United States alone, it will be seen that the cost of power for this operation is very large.

In consequence, as would be expected, beating has been the subject of many published articles and debates, some of the more important of which are reviewed later, but there is, even yet, no unanimity concerning the nature of the cellulose-water relationship in beating. (The sorption of water by cellulose is further discussed in Section G of this chapter.) However, it is now generally conceded, contrary to the opinions vigorously

maintained by several of the leading chemists in the field of pulp and paper until the middle twenties, that the cellulose as a whole does not undergo reaction with formation of a true hydrate in the chemical sense when it is beaten. Perhaps the most conclusive evidence of this is found in the inability to obtain any appreciable differences between the moisture content of beaten and unbeaten pulps when placed in the same atmospheric surroundings and also in the continuity of the drying curves of well-beaten pulps.[1, 2, 3] Further viewpoints on this subject are treated in Section A of this chapter as well as later in this section in connection with the various theories of beating, and also in the following Section G on sorption of water and other vapors. It is widely believed that water that is very strongly held is attached directly to cellulose hydroxyls. It is clear that only those hydroxyls that are not involved in hydrogen bonding with their neighbors (p. 375) will be able to hold water firmly enough for the bond to be possibly considered as being chemical in nature. It is also evident that any hydroxyls which have their hydrogen bonds with their neighbors disrupted in the beating process thereupon will be able to bind water. It is immaterial from the standpoint of the beating phenomena whether this bound water is considered to be chemically or physically bound, as long as it is clear that it is actually attached to cellulose hydroxyls that are not otherwise engaged.

According to the data published by Weidner,[4] a spruce sulfite fiber increases about 1% in length and a little less than 10% in diameter when exposed to an atmosphere which varies between 0 and 95% relative humidity. It is also known that when fully saturated with water, dry paper-making fibers increase in diameter in the order of about 20% and in length by about 1%. The variation of water-binding capacity with the nature of the sample, and particularly with its degree of crystallinity and the content of impurities, makes it likely that much of the water is held in the noncrystalline portion of the cellulose. This is particularly borne out by the increase in dimensions of the sample on swelling in water without change of the x-ray diagram. Several theories[5] have been offered to explain fiber swelling, which is probably the result of a swelling of the amorphous intermicellar material. This phenomenon is discussed elsewhere in this book (see Sections A and G of this chapter, and p. 369 of this section).

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[1] W. B. Campbell and L. M. Pidgeon, *Pulp Paper Mag. Canada*, **29**, 185 (1930).
[2] C. O. Seborg and A. J. Stamm, *Ind. Eng. Chem.*, **23**, 1271 (1931).
[3] S. E. Sheppard and P. T. Newsome, *Ind. Eng. Chem.*, **26**, 285 (1934).
[4] J. P. Weidner, *Paper Trade J.*, **108**, 31 (Jan. 5, 1939).
[5] A. J. Stamm, U. S. Dept. Agr., *Misc. Pub.* **240** (1936).

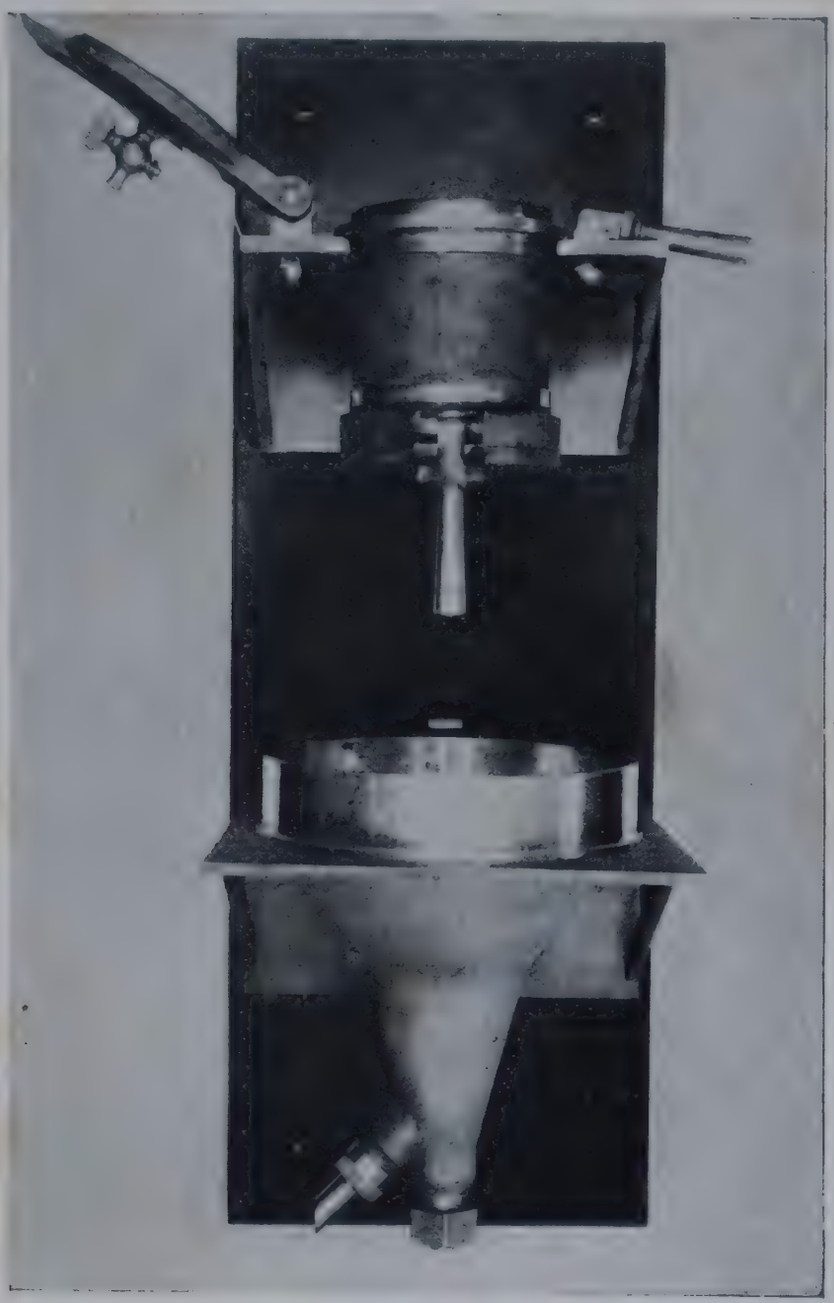
Because of economy in transportation and also resistance to decay in a dried condition, most purchased pulps (excluding groundwood, which is not easily defibered after drying) are shipped after having been dried on steam cylinders to a dryness of over 70%, usually about 90%, in which latter condition it is technically termed "air-dry." The first step in beating, although scarcely recognized as such, is the saturation of the fibers with water and their consequent swelling and softening. The fibers swell in the water at a rate which is somewhat dependent, inversely, on the extent to which they have been dried. When swollen, they become more flexible and less brittle and better withstand cutting during the violent mechanical action of beating. Pulps which have never been dried are initially much softer and more swollen than dried fibers that have been soaked in water and, in consequence, behave differently upon being made into paper, especially after only a limited beating period. The author has estimated experimentally that, in practice, a mild treatment for about one hour in a common hollander beater is required before the papermaking characteristics of a normally dried pulp, in part only, revert to those it had before being dried. This swelling of the fibers has been termed "imbibition" by some authorities and at one time was considered to be an integral part of the beating process itself, various vacuum and pressure devices being proposed and built into the beater to accelerate imbibition. However, except for the undisputed fact that the rubbing and squeezing of the pulp during the beating period serve to accelerate the sorption of water, imbibition is now commonly regarded as more or less incidental to beating provided that fibers are properly soaked before being subjected to intensive treatment.

1. Beating Equipment and Freeness Measurements

(*a*) *Measurement of Freeness*

The wetness or slowness of a sample of stock is most easily determined by measuring and recording the time it takes the excess water in a given quantity of stock, diluted and well mixed with a given quantity of water, to drain through a perforated or wire-mesh covered bottom of a cylindrical container and thus form a sheet of a given area, under a given change of head at a given temperature. The result, under standard conditions employing a standard sheet mold, is known as the "drainage time." Instead of timing the drainage, a more common, though not necessarily better, way of making the measurement is to use a freeness tester as shown in Figure 69. The tester catches the drainage water from the cylinder in

a conical funnel which is provided with a small orifice at the apex, and an outlet tube of relatively large diameter, connected a little way up from the bottom of the cone. If the stock is "slow," the water will drain slowly



Courtesy of Technical Section of the Canadian Pulp and Paper Association

FIG. 69.—FREENESS TESTER.

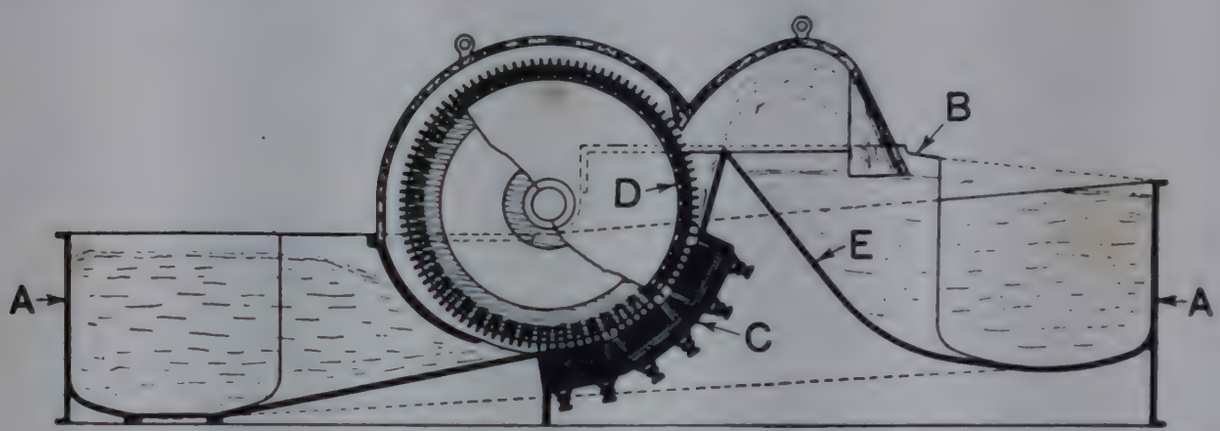
enough from the stock in the cylinder above so that the most of it will pass through the small orifice, leaving only a little to flow through the side tube. If "free," there will be a substantial rush of water during the drainage period, the most of which will flow through the side tube. The

"freeness" is measured by the number of cc. of water passed by the side tube under fixed conditions.

(*b*) *Types of Beating Equipment*

Before considering the changes of pulps effected by beating and discussing the various theories explaining them, a brief description will be given of the principles of four different typical pieces of commercial equipment in actual use.

Modern beating commenced with the introduction of the hollander about 1670. Prior to that, heavy stampers were used to break up the mass of tangled rags or fibers into a uniform pulp.



Courtesy of E. D. Jones & Sons Company, Pittsfield, Massachusetts

FIG. 70.—DIAGRAM OF A MODERN BEATER.

A. Beater tub.
B. Midfeather.
C. Bedplate.
D. Roll.
E. Backfall.

The hollander (usually termed the beater), which is still supreme in the fields of almost all but coarse papers and certain specialties, has changed but little in general design since its introduction. Figure 70 shows a cross section of a modern beater. It has the form of an oval-shaped trough A divided into two channels by a "mid-feather" B which leaves a space a little more than the width of each channel at either end. Across the bottom of one channel near the middle, is placed the "bedplate" C which is either single or multiple, as shown and is provided with projecting blades or "bars" of steel or bronze, usually from one-quarter to three-eighths of an inch thick, and spaced about the same distance apart. These blades are set at a slight angle to the plate and project from the wood spacers about one-half inch. Over the bedplate, a heavy cast iron roll D, weighing several tons and having a diameter of about twice the

depth of the trough, is mounted. The roll is also provided with blades or "bars" which are set parallel to the axis of the roll and which project about two inches. The blades are embedded about two inches apart around the circumference singly as shown, or in clumps of two or three with narrow spacers between. The bearings supporting the roll are usually at either side of the hollander and are movable up and down through a small distance so that the roll bars may be precisely adjusted so as to clear the bedplate at any desired distance from it. The bed of the trough beyond the beater roll rises sharply up from the bedplate, then abruptly slopes away, forming the "backfall" E. When the beater is in operation, the pulp suspension is circulated round the trough by the paddle action of the bars in the roll. The material is disintegrated, cut and bruised, by being caught on the edges of the bars in the form of a "fibrage" and rubbed across the bedplate bars, after which it is discharged over the backfall to flow round the trough to the front of the roll again. Usually the beater roll is "set down harder" as beating proceeds and after the fibers have become sufficiently flexible to withstand a more drastic pressure without being so readily cut. The peripheral speed of the roll is approximately 2000 feet per minute, the pulp circulates in the trough at the rate of about one revolution in two or three minutes, and the treatment is usually continued from one to a number of hours, depending on the kind of stock. The consistency of the pulp is usually from 5 to 8%. Milne's two papers[6] should be consulted for further practical information on beaters and beating.

Another common piece of beating equipment is the "jordan." This consists of a conical drum rotating in a horizontal conical casing, the rubbing surfaces being provided with blades or "knives" similar to those described for the beater. The clearance between the knives is adjusted by sliding the drum in or out of the cone. The pulp, at a consistency of from about 3 to 5%, enters the casing at the small end and is moved by both pressure and centrifugal action to the exit at the large end. These machines are built in various sizes, some having a capacity for treating considerably over 50 tons of stock per day and consuming as much as 500 horsepower in so doing. In general, the action of a jordan is more that of cutting and especially of a "clearing" of clots and fiber bundles in contrast to that of a beater, and thus jordans are now almost universally used on the stock for this purpose after the beaters and just prior to the paper machine. In the manufacture of newsprint and kraft wrapping papers,

[6] S. Milne, *Paper Trade J.*, **84**, 54 (June 16, 1927); *Pulp Paper Mag. Canada*, **37** 442 (1936).

jordans have almost entirely supplanted beaters, especially in modern mills.

Refiners have claimed some special attention in recent years. A refiner consists essentially of two large steel disks in a casing, one or both of which revolve. Like millstones, they have had bars or serrations machined into their two adjacent faces. Pulp is fed through an opening to the center of one of the disks and passes then between the faces to the outlet on the periphery of the casing. The distance between the faces of the disks is adjustable with great precision so as to vary their action on the pulp.

Rod mills, which consist of rotating steel cylinders filled partially with heavy steel rods, have also found a very limited application. The pulp, which may have a very high consistency (up to 20% or more), is fed in at one end and finds its way to an outlet at the other end, after having been subjected to the rolling and pounding action of the rods.

(c) *The Action of Beaters and Refiners*

The above four types of beating machines are representative of all pieces of equipment commercially used for beating, but there are many variations of each type in daily use. The consistency of the pulp, the bar thicknesses and the metal used in their construction, and the speeds and pressures, may be varied so widely in each of these types that the specific action of each cannot be readily characterized. It may be said, however, that, in general, the beater action is predominantly that of rubbing, the refiner or jordan that of cutting, and the rod mill that of bruising. If a beater is equipped with sharp (or thin) blades, especially if made of bronze, and the consistency of the pulp is lowered, as is commonly practiced in making blotting paper, then cutting predominates. Wide (or dull) blades and a high consistency emphasize rubbing, a condition desirable for high-class writing papers. The substitution of a stone roll (made of basalt lava with deep and wide channels cut in its face) for the usual beater roll containing metal blades will make the beater excel at bruising, which is desirable for greaseproof and glassine papers. With a given power input, a reduction of the speed of the beating elements necessitates a lesser clearance between them and, hence, the relative degree of cutting, in relation to bruising and rubbing, is increased.

2. Effects of Beating

(a) *Changes to Pulps after Beating*

When pulp (excluding in this discussion mechanical or groundwood pulp) is beaten for a sufficient length of time, the following changes take place:

1. An appreciable swelling of the fibers occurs, until they are thoroughly saturated with water. This swelling, however, does not noticeably increase with beating until the internal fiber structure is loosened.

2. A reduction in the average fiber length results. Wet fibers are not very strong and they are more or less readily cut by pressure, especially if sharp bars are used.

3. Local bruising and splitting or unraveling of the fibrous structure and the formation of fibrils visible under relatively low magnification are also noted. The manner in which the fibers split and fibrillate depends on their structure.

4. At least a portion of the primary wall or sheath that surrounds the fibers is removed (see Fig. 71, p. 373). The importance of the difference in chemical and physical characteristics of this sheath compared with those of the body of the fiber (the secondary wall) has only recently been recognized.[7,8]

5. The presence of an exceedingly fine microscopic fibrillation of fuzz on the underlying secondary wall of the fiber may be easily observed with the electron microscope or following a silvering technique,[9] by means of an ordinary microscope. It requires a good microscope and very skilful technique to make this fine structure visible without silvering. (See Section C of this chapter.)

6. The fibers become more limp and flexible in their wet state.

7. There is a rapid increase in the external specific surface of the pulp; that is, of the exposed area per unit weight of material, especially at the initial stages of beating.[9, 10]

8. A greasy or slimy feel develops when the wet pulp is squeezed in the hand. The thick pulp also flows more readily in the beater tub.

9. An increase in the time taken for water to drain away from a mass of wet pulp when placed on a screen is observed along with increased resistance to the passage of further water through the wet mat. The amount of water retained by a given dry weight of pulp under a given pressure was reported[11] to be more for a beaten than for an unbeaten pulp. Several observers, however,[12, 13] have found that the amount of

[7] F. E. Brauns and H. F. Lewis, *Paper Trade J.*, **105,** 35 (Sept. 2, 1937).

[8] J. d'A. Clark, Inst. of Paper Chemistry, unpublished work, 1941.

[9] J. d'A. Clark, *Paper Trade J.*, **115,** 32 (July 2, 1942).

[10] J. Strachan, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **13,** 61 (1932–3); **14,** 447 (1933–4).

[11] J. Strachan, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **6,** 139 (1925–6).

[12] J. H. B. Bell, *J. Soc. Chem. Ind.*, **52,** 109T, 119T (1933).

[13] A. Sedoff, C. V. Holmberg, and E. C. Jahn, *Paper Trade J.*, **109,** 42 (Dec. 28, 1939).

water retained by either pulp under pressure is the same, provided that enough time elapses for equilibrium to be reached.

10. When stirred in a dilute suspension in water, well-beaten pulps usually disperse much more readily than unbeaten pulps and, on standing, they do not floc as quickly. Fibrillation developed during beating promotes clotting of the fibers in suspension because of the resulting mechanical entanglement upon chance contact. However, this effect is usually more than offset by the concurrent reduction in fiber length during beating which gives the fibers greater freedom to move and turn in the suspension without touching each other. The addition of hydrophilic colloidal material also tends to maintain dispersion.[14, 15]

11. The electrokinetic potential of the pulp is stated to increase.[16] Because of the difficulty of making such measurements with precision and the fact that the exposed surfaces of the fibers are now known to increase greatly, as well as the possible influence of the removal of the surrounding membrane, the reported results would appear to require confirmation.

12. The effect of beating on the properties measured by cuprammonium viscosity and copper number is open to question. Some observers report that intense beating slightly reduces the viscosity of a solution of the pulp in cuprammonium hydroxide, increasing at the same time the copper number.[17] Negative results have been obtained by other observers so that, in general, it may be concluded that the effect of beating on the chemical characteristics of pulp under normal conditions is not appreciable.

13. Only very slightly, if at all, does beating increase the equilibrium moisture content of the pulp under the same atmospheric conditions,[1, 2, 3, 18] provided that possible differences caused by the effects of moisture hysteresis are eliminated. (Most cellulosic materials contain approximately one-eighth additional moisture at a given atmospheric humidity and temperature if approached from a wetter instead of from a drier state. As a rule also, the purer the cellulose, the less the moisture content under the same conditions.)

14. The sorption of most basic dyestuffs, such as methylene blue, in aqueous solution is scarcely affected,[10, 19] but with certain direct dyes, such as Purpurin 4B, and also alumina sol and other positive colloids, some

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[14] J. d'A. Clark, *Tech. Assoc. Papers*, Ser. **19**, 383 (1936).
[15] A. Erspamer, *Paper Trade J.*, **110**, 33 (June 13, 1940).
[16] K. Kanamaru, *J. Soc. Chem. Ind. Japan*, **34**, suppl. binding, 39 (1931).
[17] C. E. Curran, F. A. Simmonds, and H. M. Chang, *Ind. Eng. Chem.*, **23**, 104 (1931).
[18] W. B. Campbell, Can. Dept. Interior, *Forest Service Bull.* **84** (1933).
[19] O. Kress and H. Bialkowsky, *Paper Trade J.*, **93**, 35 (Nov. 12, 1931).

increase in sorption does occur probably, in part at least, because of the increased external surface.[10]

15. The concentration of inert substances, such as sugar, dissolved in water into which the fibers are placed is not appreciably changed by their having been beaten.[12] This, however, is not a very sensitive method for the detection of combined water in the presence of adsorbed water.

16. The heat of wetting of dried cellulose when placed in water is not appreciably affected by beating, but crushing cellulose while dry increases the heat of wetting by about 25%.[20] This would indicate that fresh internal surfaces opened up by beating are mostly closed again on drying and that the reformed bonds between adjacent micelles are not capable of being opened again by wetting. When beaten pulp is dried and repulped, it is well known that most of its beaten characteristics are lost even after being completely defibered. This also indicates that broken internal bonds of the fibers are reformed on drying.

17. The x-ray diffraction pattern of the cellulose is unchanged. It has been shown that a very drastic treatment, such as mercerization, is required to change the pattern[21] so that beating could hardly be expected to have an effect.

18. When formed into paper, the retention of precipitates and particles is increased after beating, at least until the pulp is very well beaten. This follows from an increased specific surface and from the entangling action of the fibrils produced.

19. The fibrous structure of the paper from beaten stock will shrink more on drying and give a harder, more dense, and much less porous paper. This phenomenon has been adequately explained by Campbell,[18] whose theories will be briefly discussed later.

20. The opacity of the paper decreases. Very well-beaten pulp forms a paper quite translucent and, incidentally, one less pervious to oil (*e. g.*, greaseproof paper or imitation parchment). Additional beating and heavy calendering form a transparent paper (*e. g.*, glassine). The opacity of a paper is dependent, among other things, on the extent of the solid-air interfaces present in its structure. These, in turn, depend on the total specific area of its components, less the area in solid contact. With beating, the latter increases more rapidly than does the former.

21. A given quantity of dyestuff will give an appreciably greater intensity of color to finished paper made from beaten stock. This follows from the changes noted in the preceding paragraph.

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[20] O. Maass and W. B. Campbell, *Pulp Paper Mag. Canada*, **40**, 108 (1939).

[21] C. Trogus, *Verein Zellstoff- Papier-Chemiker u. -Ingenieure, Jahresber.*, **1928**, 140.

22. The degree of sizing of paper (*i. e.*, resistance to aqueous fluids), with a given quantity of sizing material, such as rosin size and alum, improves markedly. In practice, very well-beaten stock, such as that prepared for glassine, is very difficult to size, probably because of the very low retention of added materials other than sugars or polysaccharides. Even starch is poorly retained.

23. The paper will have a higher tensile and bursting strength and will stretch more before rupture. Excessive beating may reduce the bursting strength from its maximum value but seldom the tensile strength.

24. Except for a rise in the resistance of the paper to tear as is frequently observed during the early stages of beating in practice, the tearing strength progressively diminishes.

25. The ability of the paper to withstand repeated folding rises to a maximum, then usually diminishes rapidly.

The underlying reasons for these and other changes in the physical qualities of the paper with beating would involve a discussion of the nature of the tests for those qualities, which is outside the scope of this chapter.

(*b*) *Other Beating Phenomena*

The following additional observations have been made concerning the process of beating.

1. The rate of strength development of the paper into which the pulp is formed is considerably greater in the early stages of beating. As beating proceeds this rate of increase gradually falls to zero or the strength may reach a maximum and then even diminish.

2. It is well known that impure fibers, for example, unbleached pulps and especially ordinary straw pulps, because of their high hemicellulose content, beat more rapidly than purer fibers. The pentosan content of the pulps appears to have a marked influence on beating.[22] Bleaching as a rule removes some of the hemicellulosic materials, especially if the pulps have been treated with a caustic extraction during the bleaching process. A mercerized or highly purified pulp, containing a high alpha-cellulose content, is exceedingly difficult to beat.[23] On the other hand, rag pulps which have the same or a higher alpha-cellulose content, especially if from well-worn materials, are not so difficult to beat. An explanation of this may probably be found in the different manner in which the various fibers disintegrate under the action of the beater. Cot-

[22] G. H. Young and B. W. Rowland, *Paper Trade J.*, **97**, 44 (Oct. 12, 1933).

[23] G. A. Richter, *Ind. Eng. Chem.*, **23**, 131, 266 (1931).

ton and especially bast fibers, such as linen, are frayed out and unraveled into a mass of very fine, long fibrils by beating, whereas beating special wood and similar pulps having a similarly high alpha-cellulose content results in the fibers breaking up into relatively coarse short particles, or at best into coarse fibrils. In consequence, linen pulp is preferred for the highest quality products, such as currency, cigaret, and condenser papers.

3. If a pulp is hydrolyzed (*e. g.*, with a mineral acid), the treated pulp beats more rapidly, especially if the cuprammonium viscosity falls below about 10 centipoises (1% solution).[24] A pulp prepared by the sulfite process (acid) with a moderate degree of cooking, as determined by its bleachability, beats more rapidly than a pulp prepared by an alkaline cook (*e. g.*, soda or sulfate) to the same degree of cooking. Mitscherlich pulp (pulp prepared by a relatively mild slow sulfite cook) beats still more rapidly. These facts also are partly explained in the preceding paragraph and are further discussed later in this chapter. Strachan[25] has given added explanations for the behavior of these pulps, based on changes in the structure of the fibers influenced by the different cooking processes.

4. An increase in the temperature of the pulp decreases the rate of beating; conversely, low temperatures promote more rapid beating.[26] Also, when beaten stock is heated, especially to a high temperature, its wetness is considerably reduced.[27] These effects, which have been well known in practical papermaking for a long time, are both probably concerned with the fact that the swelling of pulps in water is appreciably exothermic.

5. Contrary to the findings of Nikano, as discussed by Le Compte,[27] Clark[28] has found that the strength and other qualities of the resulting paper are not impaired by heating a beaten stock. Also, the wetness of the stock is not recovered by afterwards soaking for a long period, for example several days, but it may be recovered, at least in part, by stirring the stock vigorously at normal temperatures.

6. Keeping moist beaten stock sterile and wet for months at normal temperatures does not appear to alter its character.[29] However, keeping

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[24] D. M. Musser and H. C. Engel, *Paper Trade J.*, **113**, 31 (July 10, 1941); **114**, 29 (Apr. 9, 1942).

[25] J. Strachan, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **19**, 171–81, especially p. 174 (1938–9).

[26] A. Noll, *Papier-Fabr.*, **35**, Tech.-wiss. Tl., 393, 401 (1937).

[27] T. R. Le Compte, *Paper Trade J.*, **93**, 42 (Oct. 1, 1931).

[28] J. d'A. Clark, *Paper Trade J.*, **97**, 25 (Dec. 28, 1933).

[29] *Second Report of Pulp Evaluation Committee to the Technical Section.* Paper Makers' Assoc. Gt. Brit. & Ireland, London, 1936, especially p. 85.

beaten pulp for a day or two in a stock chest (*i. e.*, a large vat), where it is subject to bacterial action, usually reduces its wetness and makes it work freer on the paper machine; keeping unbeaten stock in a chest under the same conditions results, as a rule, in its beating faster and thus its working wetter with a given amount of beating treatment.

7. The incorporation of any filler, such as China clay, in any pulp, causes a reduction in the strength of paper made from it. The addition of oils and waxes and especially tannin[30] has a very marked effect in this respect. On the other hand, unless the pulp is very highly beaten, the addition of certain hydrophilic materials, such as locust bean gum, cooked starches, and gelatin, improves the strength of the resulting sheet.

In order to explain the various known effects of beating, hypotheses have been offered which may be divided into two or possibly three groups: chemical, physical, and colloidal. Associated with these differing views, respectively, are the names of Carl Schwalbe,[31] James Strachan,[10, 11, 25] and W. Boyd Campbell,[18, 32] whose main theses may be found in the references noted. Also among the more comprehensive papers on the subject are those of Bell,[12, 33] Cottrall,[34] Harrison,[35] and Kress and Bialkowsky,[19] and extended treatments of special phases of the problem by Katz,[36] and especially Stamm,[5] and the reviews of the subject by Simmonds,[37] Rowland,[38] and Clark.[28]

3. Explanations of the Effects of Beating

(*a*) *The Chemical Theory of Beating*

The chemical theory of beating, which was held by such prominent investigators as Cross and Bevan,[39] Sindall,[40] and later championed especially

[30] H. P. Dixson, Jr., *Paper Trade J.*, **111**, 29 (July 18, 1940).

[31] C. G. Schwalbe, *Paper Trade J.*, **72**, 58 (Mar. 3, 1921).

[32] W. B. Campbell, *Paper Trade J.*, **100**, 35 (Feb. 14, 1935).

[33] J. H. Bell, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **15**, 401 (1934–5).

[34] L. G. Cottrall, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **14**, 241 (1933–4).

[35] H. A. Harrison, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **11**, 303 (1930–1).

[36] J. R. Katz, *Cellulosechem.*, **11**, 17 (1930).

[37] F. A. Simmonds, *Paper Trade J.*, **101**, 35 (July 18, 1935).

[38] B. W. Rowland, *Paper Trade J.*, **101**, 98 (Sept. 26, 1935).

[39] C. F. Cross and E. J. Bevan, *A Text Book of Papermaking*. 5th ed., Spon, London, 1920, especially Chap. VII.

[40] R. W. Sindall, *The Manufacture of Paper*. Constable, London, 1908, especially Chap. IX.

by Schwalbe,[31] suggested that, during beating, the fibers were cut and fibrillated and at the same time a cellulose hydrate or slime, which was presumed to be a chemical compound of cellulose and water, was formed round the particles and provided a strong adhesive which, when dried, cemented the structure together. It is true that Cross and Bevan were somewhat noncommittal about whether or not a true cellulose hydrate was formed, and chose to term it a "physicochemical" combination, but both Schwalbe and Sindall found experimentally that beaten pulp was slightly more hygroscopic than unbeaten pulp and, accordingly, believed that some hydrate was formed. In recent years very precise measurements[3, 18] of the equilibrium moisture content of the same pulps, both beaten and unbeaten, have disclosed that the former usually, but not always, do contain more moisture, that is, up to 4% of the total moisture present. However, as Cottrall[34] has pointed out, it is very difficult to prove or disprove the formation of a very small quantity of hydrate after beating in the presence of a relatively large proportion of adsorbed water. Furthermore, because of no definite experimental evidence as to the presence of a hydrate, the slight excess of moisture in the beaten pulps may be very satisfactorily explained on the basis that intensive beating has opened up the internal structure of the fibers and provided fresh surfaces to adsorb additional moisture.

A somewhat similar viewpoint, not entirely novel, has been discussed recently by Totney.[41] It is considered, on purely hypothetical grounds, that a liquid mucilage of carbohydrate material is formed in greater or lesser quantities when water permeates a fiber and this is squeezed to the surface when the fiber is subjected to mechanical treatment. Wurz,[42] for example, has postulated that pectin-like substances, uronic acids, are a necessary content of pulps from which greaseproof papers can be satisfactorily made.

The chemical theory of beating was a very comfortable one to the papermaker as it could be made to explain satisfactorily almost, if not quite all, the more practical beating phenomena which have been referred to above. In particular, by the reasonable postulation that the hydrate was glue-like in character and increased in quantity as beating proceeded, a good explanation was provided for the characteristic way in which the strength of sheets made from cellulose fibers increased with beating. In-

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[41] F. Totney, *World's Paper Trade Rev.*, **117**, Tech. Supplement, 5, 9, 13, 17 (Feb. 6–May 1, 1942).

[42] O. Wurz, *Papier-Fabr.*, **35**, Tech.-wiss. Tl., 54, 57 (1937); **38**, Tech.-wiss. Tl., 87 (1940).

deed, Schwalbe not only proposed the use of chemical agents, such as acids and alkalies, to expedite beating by the formation of a hydrate, but he even carried out one or two apparently satisfactory commercial demonstrations.[43]

The main difficulty in securing a general acceptance of any one physical theory, on the other hand, has been the absence of an equally satisfactory and simple explanation of the mechanism of bonding as was provided in the chemical theory or by the mucilage or glue hypothesis; therefore it is with this point especially that many investigations and differences of opinion have been concerned.

(*b*) *Physical Theories of Beating*

The chemical theory was severely criticized by Strachan in 1926.[11] He insisted that the taking up of water by pulp in beating should be termed "imbibition," not hydration. He described the water content of paper stock as follows: (1) water of suspension, in which the fibers float; (2) capillary water held between the fibers and in their canals and pores; (3) colloidal water composed of (a) water of "imbibition" adsorbed by the unbeaten fiber and (b) water of "hydration" or an increase of water of imbibition due to beating. The colloidal water was stated to be held partly by adsorption and partly by occlusion.

Strachan described a number of experiments which he conducted on artificially made fibers having a density of 1.2, prepared from rag paper moistened with zinc chloride followed by thorough washing ("vulcanized" fiber), and demonstrated quantitatively the effects of vacuum, pressure, temperature, alum, acids, and alkalies on the rate of imbibition of his material, which was presumed to be analogous to the fibers of a pulp.

After describing his concept of the internal structure of the cellulose fiber, confirmed later by others,[44, 45] Strachan postulated that the layers of compacted fibrils, being porous, allow water to penetrate and thus cause the fiber to swell. When the fiber is then subjected to the beating action, the outer layers are loosened, and the surface becomes fibrillated, there is easier access of the water to the inner layers, and the rate of water penetration is thus increased. He considered that beating increases the

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[43] C. G. Schwalbe, *Paper Trade J.*, **80**, 46 (Jan. 22, 1925).

[44] G. J. Ritter and G. H. Chidester, *Paper Trade J.*, **87**, 131 (Oct. 25, 1928).

[45] G. W. Scarth and J. D. Spier, *Trans. Roy. Soc. Can.*, **23**, 281 (1929).

water content of the fibers by the dual effects of fibrillation, which enables the fibers to hold more water, and by the pressure to which the fiber is subjected. For example, increasing the consistency of pulp in a beater results in a greater effective pressure being applied and, consequently, faster "hydration" or increase in imbibition. He pointed out that only the surface of the fibers is affected by prolonged light beating, and under these conditions a strong opaque paper, such as currency paper, is obtained; whereas, if the fibers are subjected to intensive beating, the whole mass is bruised and softened and fibrillation takes place throughout the fibers, giving a more transparent, greaseproof type of paper. When a sheet of paper is made, the fibers of beaten stock are soft and fibrillated and lie and adhere together more closely on the forming wire of the paper machine. Between the press rolls, the fibers are squeezed and are drawn in intimate contact according to their degree of plasticity and degree of fibrillation. As the fibers are dried, the water of imbibition is forced out and they shrink. The outer layers of the fibrils on the fibers also shrink together, so that the dried fibers become coated with a layer of denser structure than was previously the case. The fibers are no longer as porous as they were before beating, because the air spaces have been largely closed, producing hardness and transparency in the mass. The compacting of and cohesion between the fibers, finally, is somewhat increased by the subsequent calendering. During the process of beating, some of the fibrils become detached from the fiber; Strachan held such material to be useless from the papermaking point of view. He assumed adhesion between the fibers to be caused primarily by the mutual entanglement of the fibrils produced by beating, the detailed mechanism involved being described merely by a statement that it is in accordance with "well-known physical laws."

Strachan's explanation of the beating action was held by several critics[46] to be incomplete in a number of particulars. Some exception was taken to his denial of the existence of a true cellulose hydrate, such as has already been discussed, but more important was the fact that his theory did not explain the marked increase in strength obtained in paper made from pulp which was given only a mechanical stirring treatment in water, even though previously the pulp is thoroughly soaked. Strachan, however, claimed that even with such a slight treatment, an exceedingly fine degree of fibrillation, which was sufficient to account for the increased strength, actually occurred. Cottrall pointed out that a thorough wetting

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[46] *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **13**, 1 (1932–3).

of a felted wool fabric did not destroy its strength as did the wetting of paper, so that in any case the mechanism of bonding could not be merely that of fibrillar entanglement. However, it must be admitted that water does not soften wool as it does cellulose.

The work of Kress and Bialkowsky[19] further confirmed the observation that no appreciable chemical changes occurred with beating except an increase in the sensitiveness of the pulp to hydrolysis and a slight decrease in the cuprammonium viscosity, effects which may be ascribed to mechanical changes. They noted that a beaten pulp sorbs no more methylene blue dye from an aqueous solution than an unbeaten pulp. Although methylene blue is positively charged in solution, it appears to be able to penetrate the intermicellar structure of the cellulose quite easily.

This finding was later confirmed by Strachan[25] and was held by him to prove that the total (*i. e.*, including the internal) specific surface of the cellulose was not increased by beating. Strachan[10] also showed that the retention of positively charged sols like silver oxide, especially when precipitated in the presence of pulp, increased markedly as beating progressed, which indicated an increase in the external specific surface. This proved to be in conformity with the developed wetness as measured by a freeness tester.

Kress and Bialkowsky furthermore reported the results of a number of experiments with pulp and various organic liquids. They measured the swelling action of the different liquids on cellulose and found that the swelling power corresponded with the degree of beating obtained and with the strength developed in the resulting paper, when cellulose was beaten in that liquid. No strength or swelling was developed in oil, very little in alcohol, considerable in ethylene glycol and in water, and still slightly more in formamide. No visible fibrillation was developed in oil or alcohol, even after intensive beating. They conclude that "these physical changes are mainly occasioned by the swelling of the fibers by the liquid in which the stock is beaten, with the result that there is an increase in the volume of the fibers. In the wet swollen condition, the fibers are low in strength but are highly plastic and ductile and any mechanical action will tend to bruise and fibrillate the fibers rather than to produce a sharp cutting action. The hard close nature of the paper made from so-called hydrated stock seems to be due entirely to the fibrillation of the fibers and the shrinkage of the fibers when the liquid producing the swelling and shrinking is removed by drying."

It will be noted that this conclusion is in accord with that previously reached by Strachan.

(c) *Partial Solubility of Cellulose*

A different view of the mechanism of bonding was presented by Campbell in 1932,[47] and most of the subject matter in this and some later articles on the subject were published in the pamphlet[18] previously mentioned in connection with moisture equilibria.

A few years previously, Urquhart[48] had advanced the hypothesis that, during the formation of cellulose, a precipitate was formed in the presence of water and, hence, the hydroxyl groups would have some molecules of water attached. As the fiber dried, the hydroxyl groups would be freed from water and their residual valences would be extensively satisfied by those of adjacent cellulose molecules. When the fibers were again wetted with water, some of these bonds would be broken and some of the hydroxyl groups would reattach themselves to water, giving a looser form of structure. If this water is driven off again, the groups once more mutually bind together. This concept was accepted and extended by Campbell who suggested that, because of their "partial solubility," the molecules, especially the short-chain molecules, when exposed on the surface of a fiber by beating, were on the verge of solution.[49] They were thus endowed with a freedom that enabled the molecules of adjacent fibers to so orient themselves that, upon drying, many of their hydroxyl groups could bind together by means of secondary valence forces.

In connection with "partial solubility," Wislicenus and Gierisch[50] found that, after breaking down pure cellulose fibers by very fine dry grinding, up to 0.4% of the resulting powder became soluble in water and, because the amount of ash in the dissolved portion was little more than in the original paper, it was clear that part of the cellulose itself had dissolved; chemical tests indicated that the dissolved material had undergone considerable degradation. Recently Strachan[25] published data to show that appreciable (though very small) quantities of material, from 13 to 21 parts per million, were dissolved by cold water from a carefully purified cotton cellulose, even after as many as fifty extractions. Upon evaporation, the hydrolyzed residue had a reducing action equivalent to about 15% of its weight of glucose. Also, in a discussion of Strachan's paper,

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[47] W. B. Campbell, *Paper Trade J.*, **95**, 29 (Oct. 25, 1932).

[48] A. R. Urquhart, *J. Textile Inst.*, **20**, 125T (1929).

[49] The concept that individual cellulose chains may be partially in solution or swollen and partly attached to the solid residue is amplified in Chapter IX, A.

[50] H. Wislicenus and W. Gierisch, *Kolloid-Z.*, **34**, 169 (1924).

Turner[51] described experiments he had carried out by dipping a highly purified cotton fabric in conductivity water. The brown line formed where the water evaporated consisted of material which was soluble in alcohol and which possessed considerable reducing power. The line could be reformed at lower and lower levels on the same piece of cloth with undiminished intensity, which indicated that, by some chemical change, the cellulose was being transformed into a water-soluble material.

There thus exists some indirect experimental support for the idea of "partial solubility" of the cellulose surfaces in water as expressed by Campbell and that some of the molecules on the surface are on the verge of, or are even completely in, solution, especially those molecules of cellulose and allied materials having a relatively short chain length. Furthermore, it has been shown that a completely acetylated pulp has little strength if made in water but has considerable strength if formed in alcohol or acetone in which it is partially soluble.[52] Also, partial methylation[53] or partial acetylation[52, 54] under carefully controlled conditions appreciably increases the strength of paper formed from the pulp. Clark[8] has ventured an opinion that essentially the primary hydroxyl groups are involved in the linkages holding the cellulose structure together. This structure cannot readily be broken by water, but if these linkages are disturbed by the primary hydroxyl groups becoming either loosely engaged with cuprammonium complexes or xanthates or by being converted to carboxyl, ester, or ether groups, the material becomes much more hygroscopic and even soluble in water, provided that most of the secondary hydroxyl groups are left intact and are not transformed to hydrophobic radicals. This, statistically at least, appears probable during the early stages of conversion.

(*d*) *The Mechanism of Bonding*

Campbell[18] also showed by calculations that, especially with the finer fibrils, as the water is removed, the normal surface tension forces, which amount to about 140 dynes per centimeter of fiber irrespective of diameter, give rise to enormous compacting pressures, which further increase the surface areas in contact. This explains why well-beaten stock compacts so easily on drying, giving a hard, dense, strong paper.

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[51] H. A. Turner, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **19**, 182 (1938–9).

[52] J. C. Bletzinger, Inst. of Paper Chemistry, unpublished work, 1940.

[53] G. Jayme and A. Froundjian, *Cellulosechem.*, **18**, 9 (1940).

[54] W. H. Aiken, Inst. of Paper Chemistry, unpublished work, 1941.

Campbell concluded that, when fibers have access to moisture, a layer of water is adsorbed on every exposed crystal surface and a layer of hydrated cellulose (in a colloidal sense) is thus produced. The association of the hydroxyl groups with water lowers the attraction of the crystallites for each other along the natural crevices and cleavage planes in the fiber, the interior of which, it will be recognized, is normally under tension from having been dried, so that small passages are opened and additional water enters, resulting in further adsorption and swelling. Beating bends and stresses the swollen and softened structure and the fiber becomes still more flexible. Fibrillation also occurs, greatly increasing the external surface of the fibers. When the fibers are made into paper and the water is removed, the extent of bonding depends on the flexibility of the fibers and the amount of surface exposed, both being clearly dependent upon the degree of beating. The degree of orientation of the crystallites in contact with each other, which also depends somewhat on flexibility, is an important factor in the degree of bonding; thus, if the crystallites happen to be parallel and point the same way when they come together, the degree of bonding will be at its maximum.

In practice, there is a range of bonding from the slight bonding shown in blotting paper (which is both weak and opaque), to the extreme case of glassine paper where the transparency, degree of bonding, and water insolubility of the bonds are at a maximum for paper.

This explanation of the process of bonding, akin to the phenomenon of crystallization, was at variance with the conclusions of Strachan,[10] who took exception to it on the ground that the union of crystal surfaces demanded that the surface must be either malleable or liquid (*e.g.*, dissolved), so that the crystal surfaces could be oriented similarly. He stated that the first condition was obtained to a limited extent in the parchmentizing process (of vegetable parchment) and the second in the case of making cellophane, but neither condition was fulfilled with cellulose under normal papermaking treatments. He re-emphasized his opinion that "during beating, the surfaces of the fibers are rendered plastic by fibrillation. The fibrils of the two beaten surfaces become entwined and bind together. We have not only intertwining of the fibers themselves, but also intertwining of minute fibrils . . . As the external surface of the fibers increases with beating, so the cohesion between such surfaces increases in the presence of water which brings them into contact."

However, Strachan's grounds for insisting upon that mechanism of bonding exclusively disappeared when Clark[28] published his findings of the surprising shear strength developed by the bond formed when two

sheets of normal cellophane, which certainly were not fibrillated, are wetted and then pressed and dried together. He also showed that molecular orientation, as Campbell had suggested, played an important part in their adhesion.

Harrison, in the course of several contributions as a result of many careful experiments on beating,[35] published[46] some photomicrographs showing mildly beaten fibers apparently devoid of fibrillation which nevertheless formed quite strong sheets of paper and concluded that fibrillation is not alone responsible for strength. Indeed, he pointed out that, when fibrillation becomes pronounced after much beating, the rate of strength development is then barely increasing. Edge[55] showed that, when fibrillation was developed by beating a pulp in toluene, if the toluene was then displaced by water and sheets were formed, only a small fraction of the normal strength was obtained as compared with both beating the pulp and forming the sheets in water.

Bell[12] gave an account of an extensive series of experiments dealing with the drainage, shrinkage, and properties of masses or cakes of beaten and unbeaten pulps and several liquids, together with a discussion of beating on the basis of chemical, colloidal, and physical properties of the fibers. In this and in a later paper[33] where the question of adhesion is further discussed, he concluded that "Sheet strength must be due to a loose chemical bonding between the fibers . . . and is probably affected through the free hydroxyl linkages in the outer transverse surfaces of the cellulose micelles . . . . Beating exposes . . . a greater external surface with its quota of free hydroxyl groups. If, however, we can obtain sheet strength without much fibrillation, there must be some other way of liberating these hydroxyl linkages during beating." He then suggested that the actual existence of the Lüdtke[56] noncellulosic membrane system, enclosing the fiber elements, and its rupture, would account for this, and was inclined to think that fibrillation played a subordinate part.

(*e*) *The Specific Surface of Pulps*

It will be noticed that, with the possible exception of the mucilage-formation hypothesis which has no valid experimental basis at present, none of these theories accounts satisfactorily for the considerable rate of increase of strength always noticed during the preliminary stages of beating. The

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[55] S. R. H. Edge, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **16**, 273 (1935).

[56] M. Lüdtke, *Cellulosechem.*, **13**, 169, 191 (1932); **14**, 1 (1933).

author further investigated the problem recently,[8] after devising a method for depositing a fine film of metallic silver on cellulose fibers. This enabled measurements of the specific surface of pulp to be made with a

FIG. 71.—PORTIONS OF TWO BLEACHED WESTERN HEMLOCK FIBERS FROM SULFITE PULP AFTER LONG STIRRING AND AFTER BEING LIGHTLY SILVERED.

satisfactory degree of accuracy and a study of the increase of surface with beating. Incidentally the silvering technique developed also enabled the finer structure of the beaten fibers, including the minute fibrils described by Strachan, to be observed with ease.

Figure 71 shows an interesting microphotograph of two bleached sulfite fibers from a sample of pulp which was subjected to rapid stirring only, at 3% consistency for about 100 minutes, corresponding to a very mild beating treatment. A very thin film of silver was then deposited on the fibers, just thick enough to cover the fibrils and make them visible and also to reveal structural details of the loosened primary wall material which, because of its thinness, is very difficult to see under usual conditions. This sheath, which apparently has less reducing power than the body of the fiber, at this stage of silvering, is colored a golden yellow by transmitted light, whereas any fibrils on the secondary walls are almost opaque. Impressions of the bordered pits may be seen on the loosened sheath on one of the fibers in Figure 71. Where the sheath is still on the fiber or where it is folded over itself, there is no trace of fibrils or fuzz on its surface, whereas, on the other fiber, the skin of which apparently has been rubbed off, there is a uniform covering of very fine fuzz. Without the silvering operation, this fuzz is exceedingly difficult to resolve and requires a microscope with a high numerical aperture and critical illumination. The presence of the fine fuzz on the body of the fiber and its absence on the sheath have since been confirmed with the electron microscope. It is this fuzz which Strachan maintained was present on lightly beaten fibers. However, neither he nor others have mentioned the removal of the primary wall or sheath during beating, nor its freedom from fuzz or fibrils prior and subsequent to its removal.

By relating the action of a known weight of silvered fiber in the catalytic decomposition of a standardized dilute solution of hydrogen peroxide with the action of a measured area of cellophane sheeting also silvered, or silver foil, it was found that the external specific surface of the pulp increased in proportion to the logarithm of the amount of beating, that is, very rapidly in the initial stages of beating, corresponding closely with the rapid increase in the strength of the resulting papers in those early stages. Notwithstanding the mildness of the beating of the fibers shown in Figure 71, their specific surface was 36% higher, and the tensile strength of sheets made from them 270% higher, than before treatment.

(*f*) *A Composite Hypothesis of Beating*

Considering these new observations with those of others, especially of Strachan and Campbell and Bell, the following modified hypothesis of beating has been formulated:

During the chemical and mechanical treatments involved in the prepara-

tion of pulp, the primary wall of the fiber, which is permeable to but is not swollen by water, is partially cracked, rubbed loose, or removed to expose some of the underlying surface of the fiber.

When water enters the secondary wall (body of the fiber), it causes it to swell to almost the original size it had in the living plant by penetrating between the micelles, probably by bridging and breaking bonds between the secondary hydroxyl groups and perhaps a very few of those involving the primary hydroxyl groups.

The rubbing, and the partial solvent action of the water forms a kind of two-dimensional colloidal suspension of the cellulose and other carbohydrate material on the surfaces of the secondary wall, the "concentration" of which is believed to be dependent inversely on the degree of polymerization of the cellulose and allied material there situated. This state is regarded as a colloidal system in which the particles are fixed or anchored at one end but otherwise subject to all the usual laws of colloidal behavior. The surfaces of these particles, bearing hydroxyl groups, are strongly hydrophilic and attract and bind a number of consecutive layers of water molecules which, especially near the solid surfaces, are well oriented and closely packed.[20] It is this water envelope that is the so-called "water of hydration" and that gives rise to the various phenomena associated with it. The molecules of water adjacent to the cellulose surfaces are probably held by hydrogen bonding to the hydroxyl groups; if a hydrogen bond is regarded as a chemical bond, then this portion of the water may be regarded as being chemically bound.

The primary wall is not in any way water-soluble (Brauns and Lewis[7] have shown that it is even insoluble in cuprammonium hydroxide) and, therefore, whatever portion of it remains forms a protective layer on the outside of the fiber. When the fibers are almost wholly covered with this layer, as is usual in the unbeaten state, adjacent fibers in a wet web of paper are prevented from appreciably adhering together on drying, not only because of the absence of a surface "suspension" on the sheathed part of their exteriors but also because of their large diameters as compared with the diameter of fibrils subsequently produced by beating. Large diameters permit only a relatively small surface tension compressing effect on the sheet as water is removed on drying. To some extent the greater rigidity of the wet fibrous structure may be the result of the presence of part of the primary wall, and this too would prevent the fibers from coming into intimate contact when the sheet is dried.

As beating proceeds, besides rubbing off the primary wall and further wetting the fibers, the underlying material is more coarsely fibrillated,

which not only permits stronger surface tension effects to compact the sheet better, but also results in a greater extent of bonding surface. The rubbing probably also increases the "concentration" of the surface "suspensions," and any cellulosic material that is rubbed off entirely serves as an adhesive filler between the interstices of the larger fibers, similar to hexosans, pentosans, or colloidally ground cellulosic materials in the pulp. Some of the very finest material may possibly also function as a "protective colloid," forming a more stable surface "suspension" by preventing long molecules or fibrils which have been raised from the surface of the fibers from re-embedding themselves.

When beating exceeds a certain point, a state is reached where the increase in bonding material and facilities for bonding are offset by decreased fiber length and a weakening of the fibers themselves by mashing and reticulation. At this point the pulp reaches the maximum strength.

According to the composite hypothesis, all the observed facts are accounted for. It will be seen that this picture includes (1) loosening the primary sheath and underlying structural elements of the fiber, enabling interlocking of these elements, (2) deformation of the fiber so that it better fills the space allowed by its neighbors, giving a larger surface of contact within the sheet, and (3) the creation of smaller bodies which can nest in the crannies between fibers and fibrils, so further increasing contact. All three are of primary importance. This, it will be observed, is a purely physical concept. At the same time, it is pointed out that the ultimate mechanism of adhesion of the changed structure may be considered a chemical one, if we so choose to define the nature of hydrogen bonding. The great importance of water or other strongly polar compounds for this process is evident, and if we seek to interpret the facts on the basis of molecular behavior, we are driven to the concept of hydrogen bonding between adjoining cellulose chains. If the hydroxyls of these chains are highly hydrated, they do not have much residual attraction for one another. If, however, hydrated chains in close contact with one another lose their water of hydration, they will seek to establish hydrogen bonding with their immediate neighbors, whether these neighbors belong to the same or to another fiber, thus bonding the structure together. It should also be noticed that if the new bonding is between flexible fibrils and smaller elements, the sheet, on deformation, can adjust itself so that some stress is thereby placed on many bonds without overloading the most stressed. Unfibrillated surfaces will adhere strongly to one another, but the slightest movement of adjacent fibers would put large strains on the bonds due to the rigidity of

the dried fiber, and there would be a correspondingly low resistance to a breaking of the structure of a paper which depended for its strength solely on adhesion between surfaces rather than also upon interpenetration of the fibrous elements.

(g) *Some Applications of the Hypothesis*

While further experimental evidence is required to establish its complete validity, it is believed that this hypothesis explains quite well all the beating phenomena which have been recounted. Two or three of its more obscure applications, however, remain to be discussed.

The rapid initial increase in the strength of paper brought about by beating the pulp is produced by the removal of the primary wall of the fibers (which appears to come off quite easily), the consequent rapid increase of the exposed surface, and the almost simultaneous formation of the "suspension" on the newly exposed surfaces.

It will be observed that when a sheet of paper is broken, most adjacent fibers are separated not by being directly pulled apart, but by sliding along contiguous fibers. Thus, even a very slight addition to the degree of bonding between the surfaces enormously adds to the frictional resistance of the structural elements and, hence, a marked increase of the strength of the sheet results.

It is evident that freeness of pulp will be decreased by boiling, because the surface "suspension" would be dehydrated and collapse and, if we concede that the surface tension effect of the water as it is removed from between the fibers on drying is sufficient to raise the fibrils and smaller components of the "suspension," this may be the reason why boiling does not appreciably affect the strength of the resulting paper.

When pulp is produced by any mild process giving a high yield, or by an acid process which tends to hydrolyze the material, it follows that there is more short-chain material on the exposed surfaces. This will form a more "concentrated" and, hence, a more adhesive surface "suspension"; conversely, a caustic treatment, which normally removes the short-chain material, gives pulp with much less adhesiveness, because of a lower "concentration" on the exposed surfaces. At the same time, consideration must also be given to the effect of the pulping process on the strength of the fibers themselves. It follows, therefore, that pulp prepared by the mild neutral sodium sulfite process is exceptionally strong both as regards fiber structure and the presence of short-chain adhesive material. Pulp made with the normal (acid) sulfite process is weakened

in fiber structure but it, too, beats rapidly; whereas soda and especially sulfate pulps retain their fibrous structural strength to a great extent but, because of the dearth of short-chain material, beat relatively slowly.

It appears necessary to give considerable mechanical treatment to a dried pulp to make its qualities revert to those it had in a moist state, because, after drying, all the internal bonds thereby formed have to be broken and all the fibrillation and surface "suspensions" present on the cellulose-water interfaces before drying must be reformed. It is not possible to accomplish this completely, and therefore the drying of cellulose fibers constitutes, to a large extent, an irreversible process.

Because of their homogeneous structure, no artificial cellulose fibers can be "beaten" in the sense described, nor are they capable of being formed into a sheet having the characteristics of paper. Even with the addition of a large percentage of mucilage, no appreciable adhesion between the fibers can be achieved.

G. SORPTION OF WATER AND OTHER VAPORS BY CELLULOSE*

E. I. VALKO

1. Phenomena of Sorption

Cellulose and cellulose derivatives, when surrounded by an atmosphere containing the vapors of water or of some organic liquid, take up or give off the vapor until an equilibrium is reached. This behavior is a special case of the phenomenon of sorption, which is shown by most solids. The taking up of vapor is called *ad*sorption, and the release of vapor is called *de*sorption; in general, these processes do not lead to the same equilibrium, hysteresis taking place. The phenomenon is of importance because the presence of sorbed liquids changes the chemical behavior, mechanical properties, and electrical characteristics of cellulose.

(*a*) *Sorption Isotherms*

The methods of measuring sorption are well discussed in the literature.[1, 2, 3] The methods of correlating the results, however, deserve mention here. The usual one is a plot of the liquid content of a cellulose against the vapor pressure of the liquid in the surrounding atmosphere. The curves obtained are called sorption isotherms. Adsorption and desorption, of course, give different curves, and a pair of them constitutes a sorption loop.

Such a pair of isotherms for a sample of kier-boiled cotton is shown in Figure 72. The S shape of these isotherms is characteristic. In form, they differ from many other types of adsorption isotherms, particularly from

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* Translated by F. A. Lucy, Pennsylvania Salt Manufacturing Co., Philadelphia, Pa.

[1] J. W. McBain, *The Sorption of Gases and Vapors by Solids.* Routledge, London, 1932.

[2] E. Müller, *Dinglers Polytech. J.*, **245**, 210 (1882).

[3] A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, **15**, T138, T433, T550 (1924); **16**, T155 (1925); **17**, T38 (1926).

those of gases on glass or metal surfaces. Curves of the latter sort generally show a parabolic or hyperbolic form, corresponding to the Bödeker[4]-Freundlich[5] or Langmuir[6] formulas. In both these cases, a given increase in vapor pressure produces an increase in the amount of sorbed gas which is less than proportional to the vapor pressure rise. According to the Langmuir formula, the amount of sorbed gas approaches a limit asymptoti-

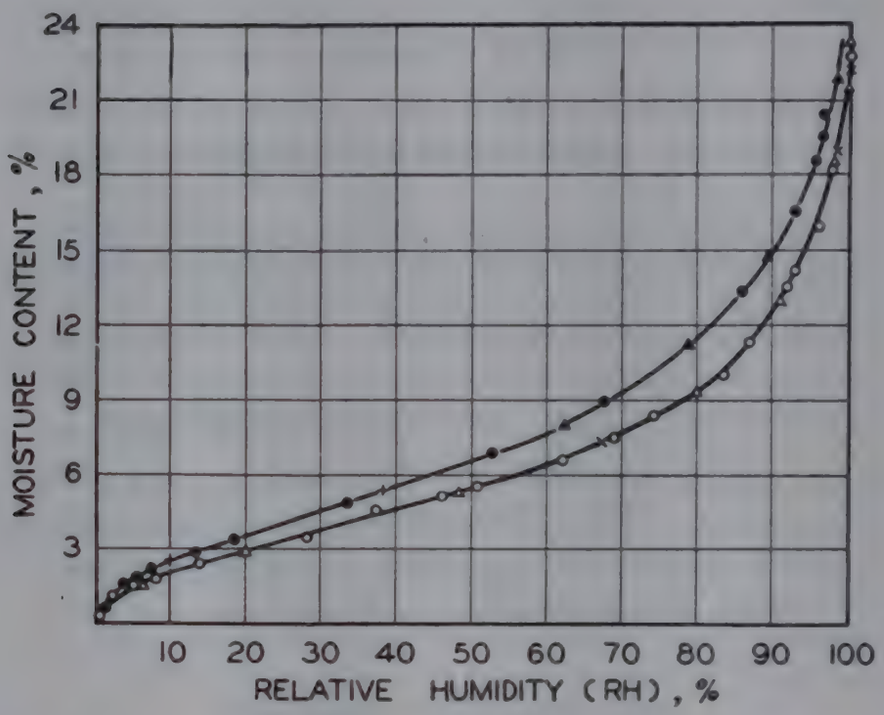

FIG. 72.—SORPTION ISOTHERMS OF KIER-BOILED COTTON (URQUHART AND WILLIAMS[3]).

Upper Curve: Desorption.
Lower Curve: Adsorption.

cally as the pressure is increased. Such behavior is actually observed for many systems. In contrast, cotton gives, for the region of high relative humidity (RH), an increase in the amount of sorbed water which is more than proportional to the pressure. The same effect is shown for systems of water vapor with numerous high polymers, including wool, silk, casein, gelatin, and other proteins. The take-up of water by sulfuric and phosphoric acids follows a similar course, as shown by Katz.[7] The sorption of

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[4] Bödeker, *J. Landw.*, p. 48 (1859).

[5] H. Freundlich, *Colloid and Capillary Chemistry.* Trans. by H. S. Hatfield from 3rd German ed., Dutton, New York, 1926.

[6] I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).

[7] J. R. Katz, *Kolloidchem. Beihefte*, **9**, 111 (1917); *Trans. Faraday Soc.*, **29**, 279 (1933).

gases near their boiling points, *e. g.*, of nitrogen on glass powder at −194°C., has likewise an S-shaped isotherm.[8] The theoretical significance of the S-shaped curves will be examined later in this section.

Cotton samples from various sources show somewhat different sorption curves. There is, further, a marked difference between the sorption of a given cotton sample before and after washing with boiling dilute alkali (as in kier-boiling). The cotton takes up less moisture after purification than before. Obviously, washing and kiering remove noncellulosic impurities of greater hygroscopicity. The differences between various samples of cotton are greater in the raw state than after purification, indicating that the raw samples differ chiefly in the amount and nature of impurities.

Various treatments have observable influence on the hygroscopicity. For instance, high-temperature drying reduces the ability of the fibers to take up water. Marked reductions also follow degradation to oxycellulose with hypobromite or to hydrocellulose with dilute sulfuric acid.[9, 10]

Of great importance is the effect on the sorption of mercerization. This effect is greater in magnitude than that of any other treatment. Ordinary mercerization increases the take-up for a given relative humidity by about 50%. A more complete description of results of experiments on this point is given in the section on mercerization (see Section D of this chapter).

Like the phenomenon of sorption itself, the hysteresis effect, which among other consequences makes the water content of a cotton sample depend on its previous history, has both practical and theoretical importance. It means, as expressed in 1906 by Masson and Richards,[11] that the observed final state of a sorption experiment is not a true equilibrium, but that the system is prevented from reaching true equilibrium either in the direction of adsorption or of desorption, or of both. The standard sorption curves, initiated, respectively, from the completely dry and completely swollen states, bound an equilibrium area. Any point on this area may be reached by starting from the correct initial state between the two extremes. As a matter of fact, the standard desorption isotherm is defined only below 80% RH. Above this vapor pressure, the equilibrium obtained depends on the maximum take-up. The take-up in saturated

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[8] P. Emmett, *Advances in Colloid Science.* Edited by E. O. Kraemer, Vol. 1, Interscience, New York, 1932, p. 1.

[9] S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.*, **33**, 1817 (1929).

[10] A. R. Urquhart, W. Bostock, and N. Eckersall, *J. Textile Ind.*, **23**, T135 (1932).

[11] O. Masson and E. S. Richards, *Proc. Roy. Soc.* (London), **A78**, 412 (1907).

atmosphere is undetermined. It is apparent from Figure 72 that at 100% RH the isotherm is almost parallel to the ordinate axis.

Recent measurements of Filby and Maass[12] are even more precise than those of Urquhart and Williams.[3] They are given in Figure 73.

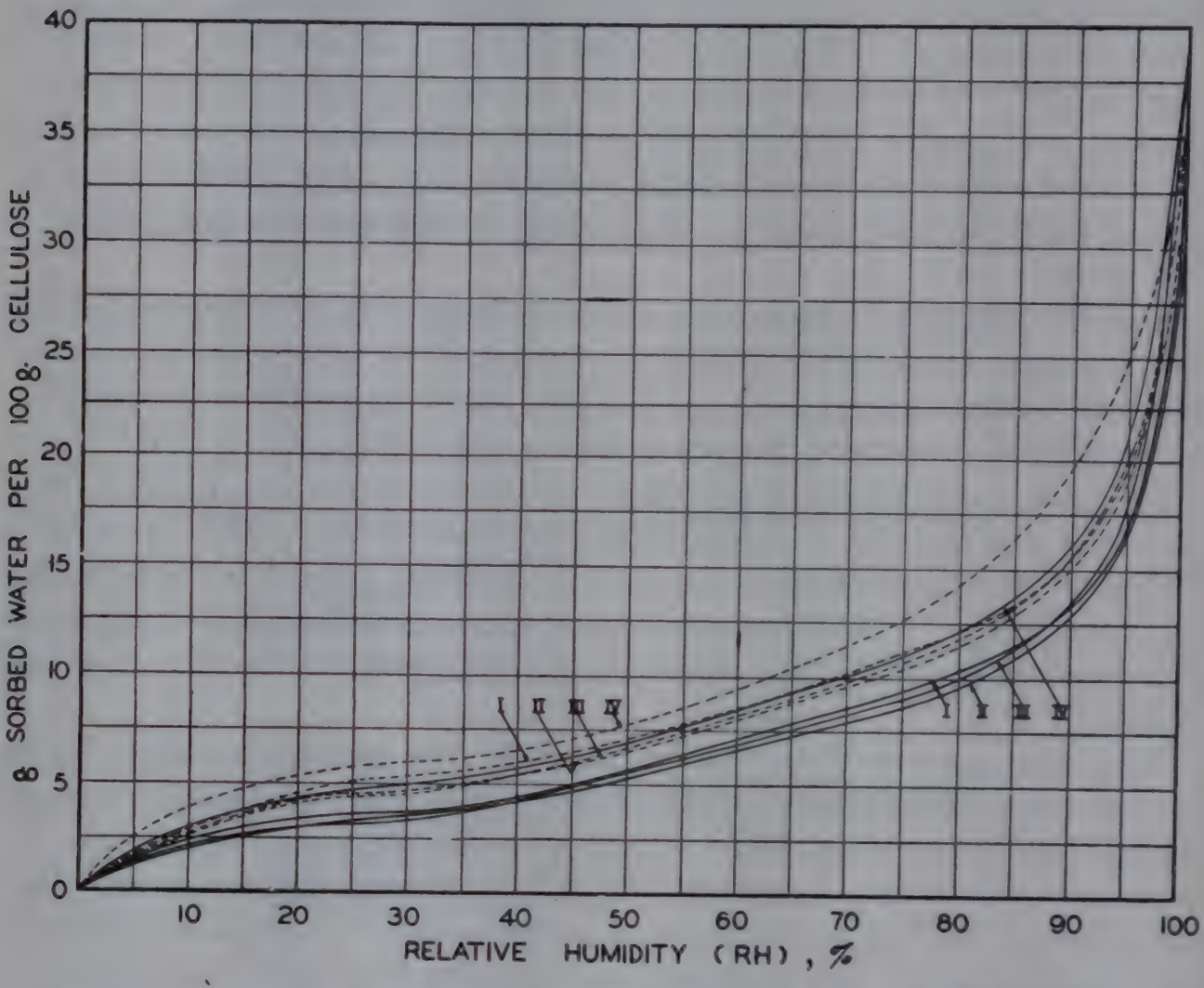

FIG. 73.—SORPTION ISOTHERMS OF CELLULOSE AT 20°C. (FILBY AND MAASS[12]).

Key: I. Standard cellulose.
II. Bleached surgical cotton.
III. Kodak rag cellulose.
IV. Bleached sulfite pulp.
——— Adsorption.
- - - - - - - - - - - Desorption.

Wood pulp, at all humidities, shows definitely higher water take-up than does cotton cellulose. Beating of pulp produces, contrary to a

[12] E. Filby and O. Maass, *Can. J. Research*, **13B**, 1 (1935).

widespread belief, no important change of sorption.[13, 14, 15] A trifling increase is, however, perceptible on exact measurement.[16]

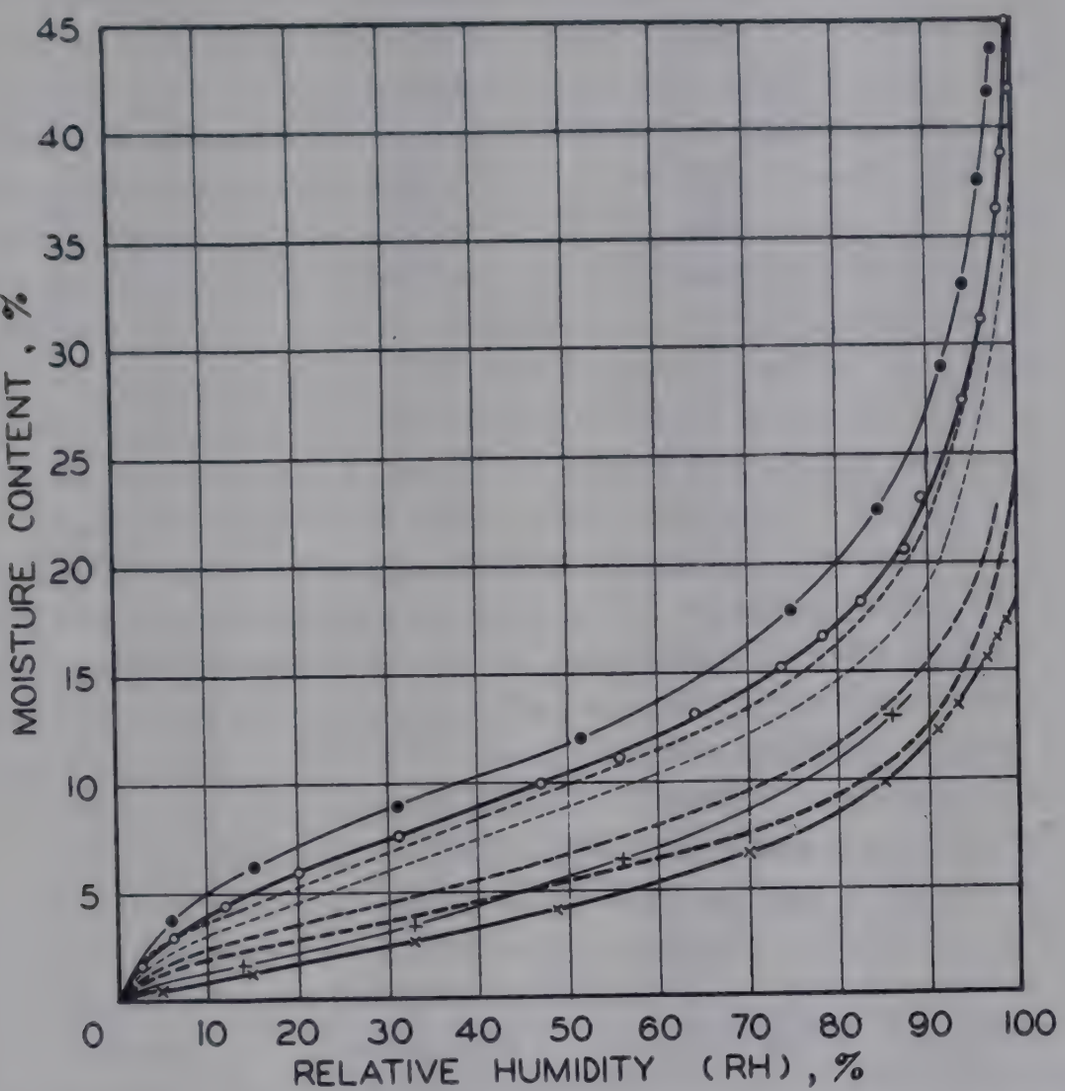

FIG. 74.—SORPTION ISOTHERMS OF CELLULOSE FIBERS (URQUHART AND ECKERSALL[17]).

Adsorption	Desorption	
——O——	——●——	Viscose rayon.
——×——	——+——	Acetate rayon.
- - - - - - - - -	- - - - - - - - -	Bleached cotton.
. . . . .	. . . . .	Mercerized cotton.

The most thorough investigation of water sorption by rayons is that of Urquhart and Eckersall.[17] It is not feasible to reproduce all their data, which cover about twenty-five different materials, including rayons made

[13] L. M. Pidgeon and O. Maass, *J. Am. Chem. Soc.*, **52**, 1053 (1930).
[14] N. H. Grace and O. Maass, *J. Phys. Chem.*, **36**, 3046 (1932).
[15] S. E. Sheppard and P. T. Newsome, *Ind. Eng. Chem.*, **26**, 285 (1934).
[16] C. O. Seborg, F. A. Simmonds, and P. K. Baird, *Ind. Eng. Chem.*, **28**, 1245 (1936).
[17] A. R. Urquhart and N. Eckersall, *J. Textile Inst.*, **23**, T163 (1932).

by the viscose, cuprammonium, nitrate, and acetate processes. Figure 74 gives some characteristic results. Arranged in order of increasing sorptive ability, the fibers are acetate rayon, bleached cotton, mercerized cotton, and viscose rayon. At many values of relative humidity, the curve for mercerized cotton differs only by a constant factor from the curve for bleached cotton (see Section D of this chapter). For rayons, the ratio is not constant. The ratio of sorption by rayon relative to that of cotton increases up to 30% RH or so, then falls. Notwithstanding the variation, the mean values of ratios such as these may be used to characterize the sorptive ability of the various fibers. For eighteen different rayons from regenerated cellulose including viscose, Lilienfeld, cuprammonium, and Chardonnet rayons, the mean values of the ratios cover the range between 1.67 and 2.12 for adsorption, and between 1.59 and 2.05 for desorption. Mean values of 1.89 and 1.84, respectively, were found for cellophane. Since the form of the curves, amount of the take-up, and hysteresis of the latter material are quite analogous to those of viscose rayon, it is obvious that interfiber spaces have no significance for the phenomenon of sorption.

It was found by Will,[18] four decades ago, that the sorptive ability of cellulose nitrate dropped with increase of nitrogen content. More recently, Sheppard and Newsome[9] treated the question of the relation between water take-up and degree of esterification of cellulose acetate. Two sorts of preparation may be distinguished: acetylation in fiber form, and acetylation in solution. Further, either natural or mercerized cellulose may be used as raw material. The authors compared sorptive abilities, which they defined by integrating the water content at varying relative humidities over the relative humidity range. The following results were found: the product prepared by acetylating natural cellulose fibers shows a linear reduction in water content with increase of esterification. Acetate either from mercerized fibers or dissolved natural cellulose has a higher water content than that of the product from the natural fibers, at least for low degrees of acetylation, but the difference falls as the acetyl content increases. This behavior is shown in Figure 75.

The reduction of sorption by acetylation or nitration is evidence of the significance of the hydroxyl group for the attachment of water to cellulosic material.

The sorptive ability of fatty acid esters of cellulose falls off with increasing size of the ester groups. At 30°C., in saturated vapor, the take-up by the triacetate is about 10%, by the tripropionate 2 to 3%, by the tri-

[18] W. Will, *Research of Cellulose by C. F. Cross and E. J. Bevan*. Longmans, Green, London, 1913.

utyrate 1.8%, and by the trivalerate 1.6%. A minimum is reached with he triheptanoate. Continued rise in the homologous series is accompanied by a slow rise in the amount of bound water.[19]

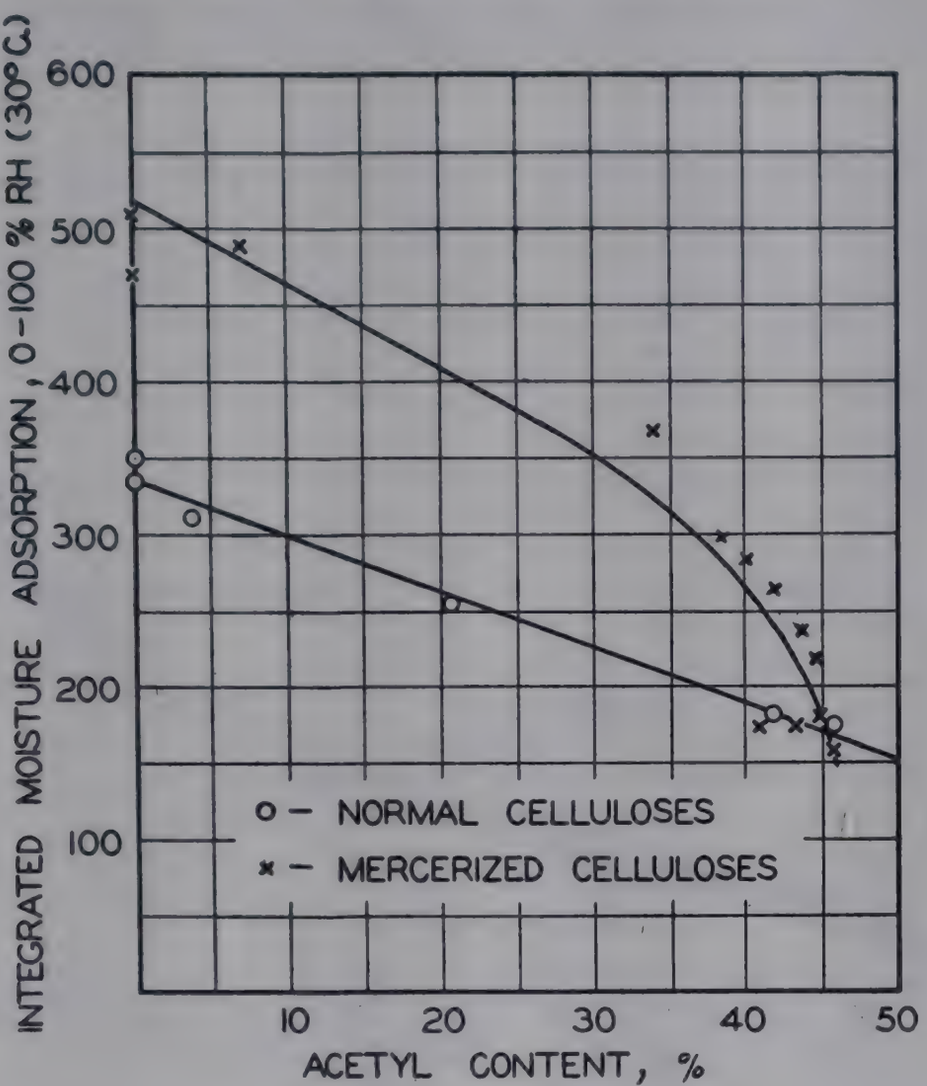

FIG. 75.—INTEGRATED VALUES OF WATER SORPTION BY CELLULOSE ACETATES AS FUNCTION OF ACETYL CONTENT (SHEPPARD AND NEWSOME[9]).

(*b*) *Temperature Dependence of Sorption*

When textile fibers are heated in a container with a definite amount of water vapor, the water content of the fiber falls by a rather slight amount, though the vapor pressure increases. Under constant absolute vapor pressure, the amount of sorption decreases rapidly with temperature increase. From the theoretical standpoint, however, greater interest attaches to the temperature dependence of sorption at constant relative

[19] S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.*, **39**, 143 (1935).

vapor pressure. In the latter case, the water content varies only slightly with the temperature. On the average, the variation is less than 1% for each 10°C., but even this slight difference has a definite theoretical significance. For cotton, the investigations of Urquhart and Williams[20] gave the following results: for a constant RH less than 80%, the moisture

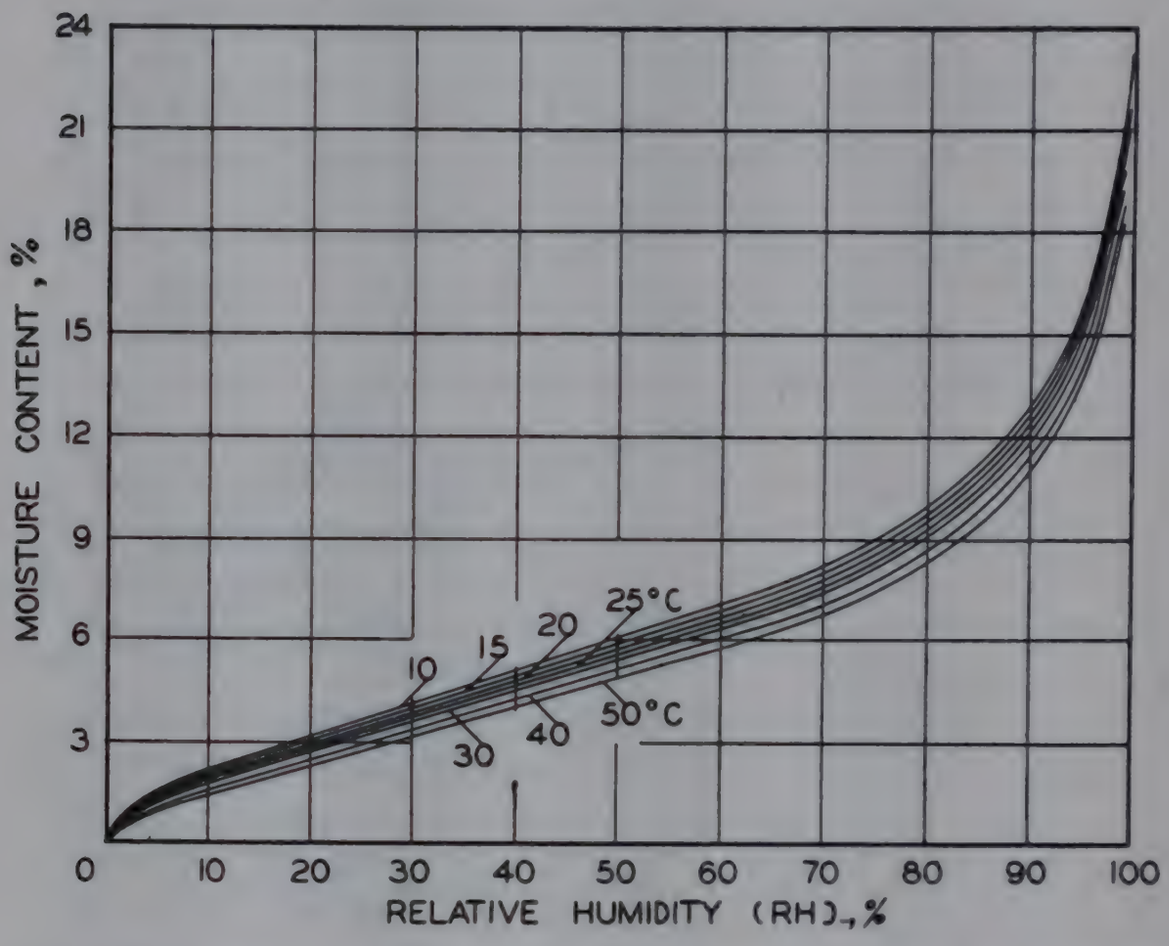

FIG. 76.—ADSORPTION ISOTHERMS OF KIER-BOILED COTTON AT VARIOUS TEMPERATURES (URQUHART AND WILLIAMS[20])

content fell on increase of temperature in the range 10 to 110°C., but for an RH over 80%, the decrease of moisture content was found only for the temperature range 10 to 50°C. Between 60 and 100°C., increase in temperature produces an increase in moisture content. These relations are expressed in Figures 76 and 77.

Newsome and Sheppard[21] investigated the temperature dependence of the water adsorption of cellulose acetate films (39% acetyl) and found that

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[20] A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, **15**, T559 (1924).
[21] P. T. Newsome and S. E. Sheppard, *J. Phys. Chem.*, **36**, 930 (1932).

the water content fell with increase of temperature throughout the entire humidity range. However, only the temperature range of 30 to 50°C. was covered.

Simril and Smith[22] determined the sorption isotherms for cellophane at four different temperatures from 16.5 to 49.5°C. The water content

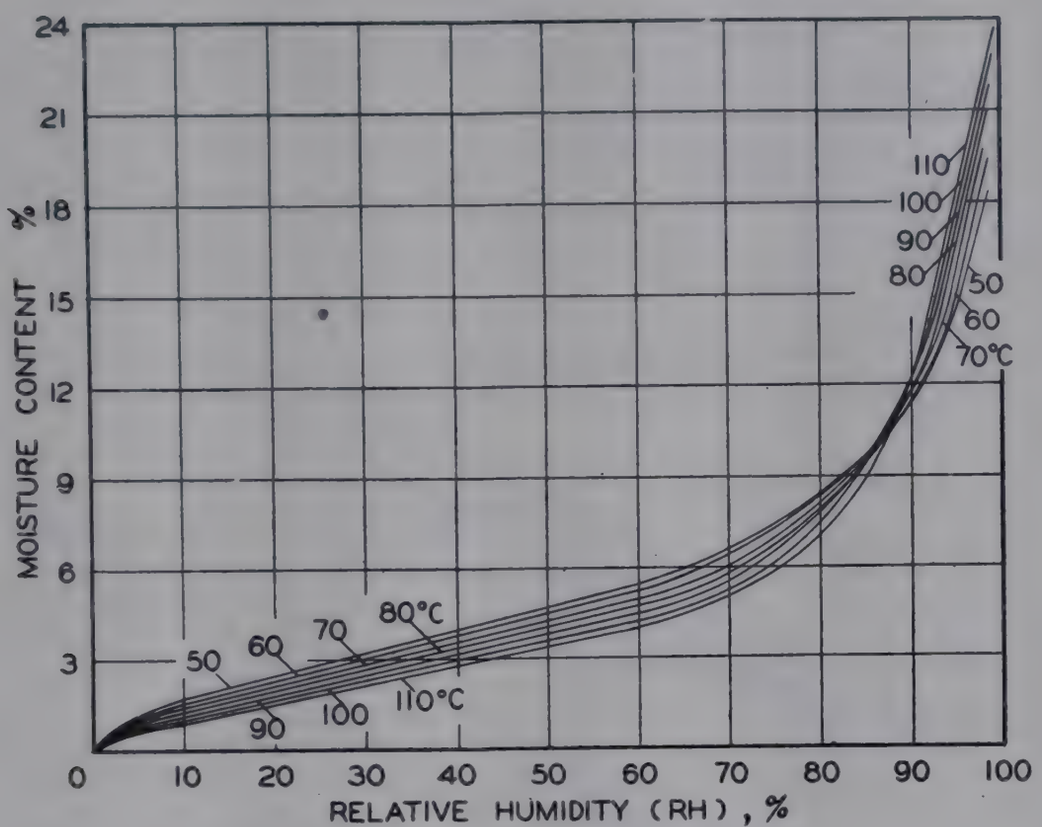

FIG. 77.—ADSORPTION ISOTHERMS OF KIER-BOILED COTTON AT VARIOUS TEMPERATURES (URQUHART AND WILLIAMS[20]).

decreased with increasing temperature, especially rapidly in the range of low humidities.

Wiegerink[23] determined the water take-up of ten different textile fibers, including raw, purified, and mercerized cotton, and viscose, cuprammonium, and acetate rayons, for temperatures between 35.5 and 150°C. Above 100°C., the relative humidity was restricted to the range in which the vapor pressure was less than one atmosphere. Adsorption, starting from the dry state, and desorption, starting from thoroughly soaked material, were determined. Figure 78 gives the results for kier-boiled cotton. Cross-over of the curves, as found at high relative humidities by Urquhart and

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[22] V. L. Simril and S. Smith, *Ind. Eng. Chem.*, **34**, 226 (1942).

[23] J. G. Wiegerink, *J. Research Natl. Bur. Standards*, **24**, 645 (1940).

Williams,[20] was not found here, possibly because above 100°C. measure ments were made only for RH below 80%. However, it may be noted tha the reduction of moisture content with rising temperature steadily becam less at the higher temperatures. Similar results were obtained for all th other materials tested. On plotting the logarithm of the water conten

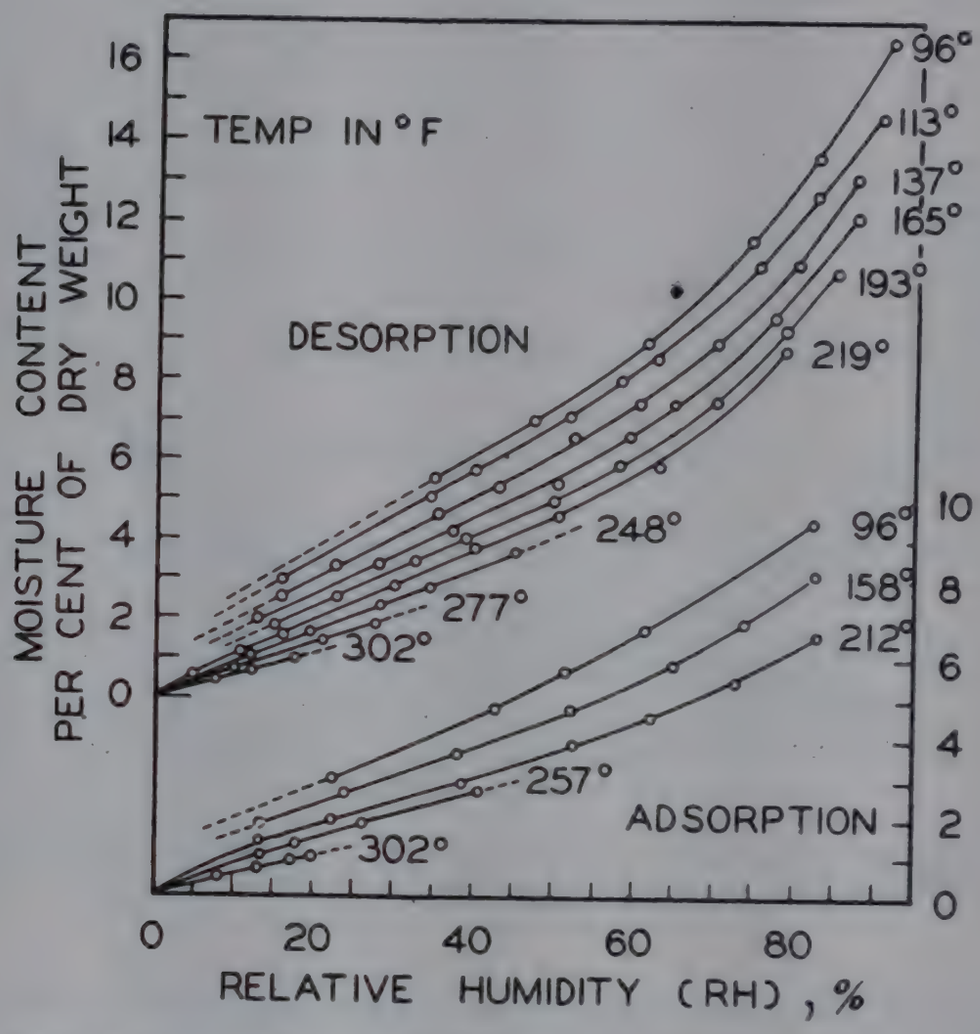

FIG. 78.—SORPTION ISOTHERMS OF PURIFIED COTTON AT VARIOUS TEMPERATURES (WIEGERINK[23]).

against the reciprocal of the absolute temperature, Wiegerink found a straight-line relation. At low relative humidities, however, the graph consisted of two lines which crossed at about 100°C.

Houtz and McLean[24] investigated the adsorption of water by linen paper between 100 and 150°C. In general, the shape of the curves found is similar to those shown above.

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[24] C. C. Houtz and D. A. McLean, *J. Phys. Chem.*, **45**, 111 (1941).

(c) *Sorption of Nonaqueous Liquids*

There are few studies of the sorption of nonaqueous liquids by fibers. Table 1 gives Brimley's[25] observations on cotton, Sheppard and Newsome's[26] values for cotton linters and alcohols, and the results of Macmillan[27] on jute. Russell, Maass, and Campbell[28] reported that bleached sulfite pulp and kraft pulp took up, respectively, about 20% and 25% of methanol. However, the degree of sorption varied in each case according to the previous history of the sample. The degree of hysteresis was greater for alcohol than for water. On desorption to zero vapor pressure, the sample retained an appreciable amount of alcohol which was not removed by continued pumping.

TABLE 1

SORPTION OF VAPORS BY CELLULOSE FIBERS

Vapor	Maximum vapor sorbed by fiber, g. per 100 g.			
	Cotton[25]		Cotton linters[26]	Jute[27]
	Unbleached	Bleached		
Water	20	21	15	32
Acetic acid	20	19	...	...
Methanol	...	...	11.2	...
Ethanol	3.5	9	8.6	...
Propanol	...	...	5	...
Butanol	...	...	1.5	...
Carbon disulfide	2	2	...	...
Benzene	2	2	...	3
Ether	7.5	7.5	...	...
Nitrobenzene	2	2	...	...
Acetone	2.5	2.5	...	20
Mineral oil	...	...	...	4
Carbon tetrachloride	...	...	...	3

Hoffmann[29] investigated the swelling of films of cellulose triacetate in organic solvents. Table 2 presents his results. Sheppard and Newsome[26] investigated the sorption of various liquids by cellulose acetate. The dependence of the adsorption of water and various alcohols as a function of the acetyl content of the fiber is shown in Figure 79.

[25] R. C. Brimley, *Nature*, **114**, 432 (1924).
[26] S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.*, **36**, 2306 (1932).
[27] W. G. Macmillan, *J. Textile Ind.*, **32**, T45 (1941).
[28] J. K. Russell, O. Maass, and W. B. Campbell, *Can. J. Research*, **B15**, 13 (1937).
[29] A. Hoffmann, Dissertation, Berlin, 1927.

Their results show the molar quantities of each sorbed alcohol as a function of the length of the alkyl group (Fig. 80).

TABLE 2

TAKE-UP OF LIQUIDS BY CELLULOSE TRIACETATE (HOFFMANN[29])

Liquid	Take-up in % by wt.
Ethylene chloride	615.4
Dichloroacetylene	293.1
Acetyl chloride	215.2
Carbon tetrachloride	14.7
Trichloroethylene	81.3
Benzyl alcohol	47.2
Benzyl chloride	37.9
Benzene	47.4
Chlorobenzene	29.9
Nitrobenzene	142.8
Toluene	27.3
o-Xylene	10.7

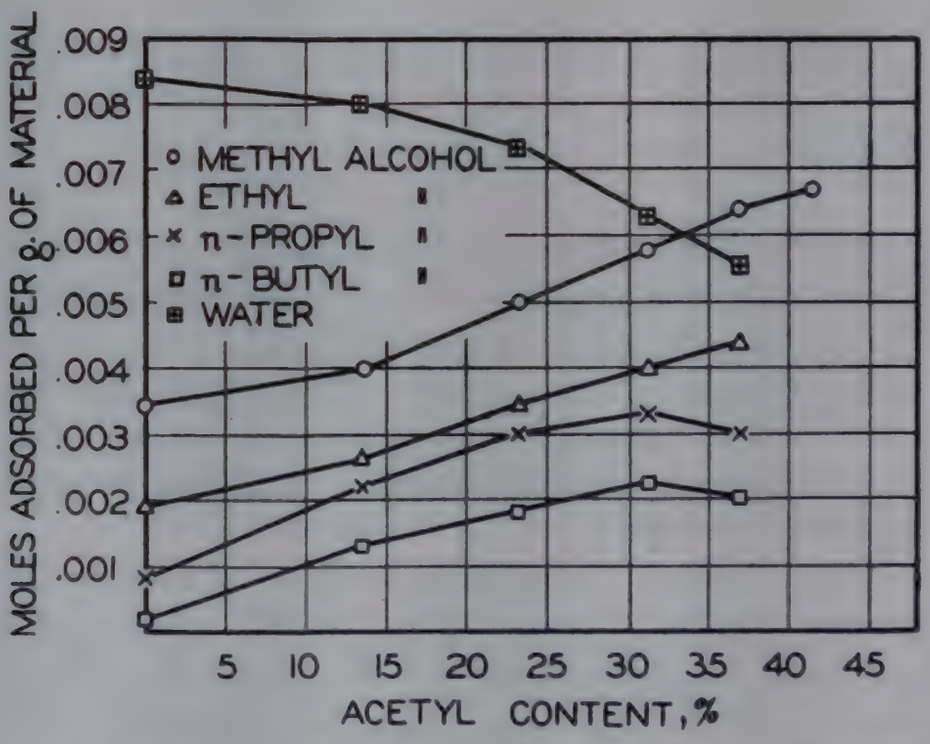

FIG. 79.—ADSORPTION OF VARIOUS ALCOHOLS BY CELLULOSE ACETATE AS A FUNCTION OF THE ACETYL CONTENT OF THE ACETATE (SHEPPARD AND NEWSOME[26]).

It appears from the results given that the hydroxyl groups of water or alcohol interact with the hydroxyls of cellulose to contribute significantly to

the sorption. Probably hydrogen bonding occurs. Acetone is also capable of forming hydrogen bonds, as are acetic acid and ether. With increasing acetylation of the cellulose hydroxyls, the interaction of alkyl

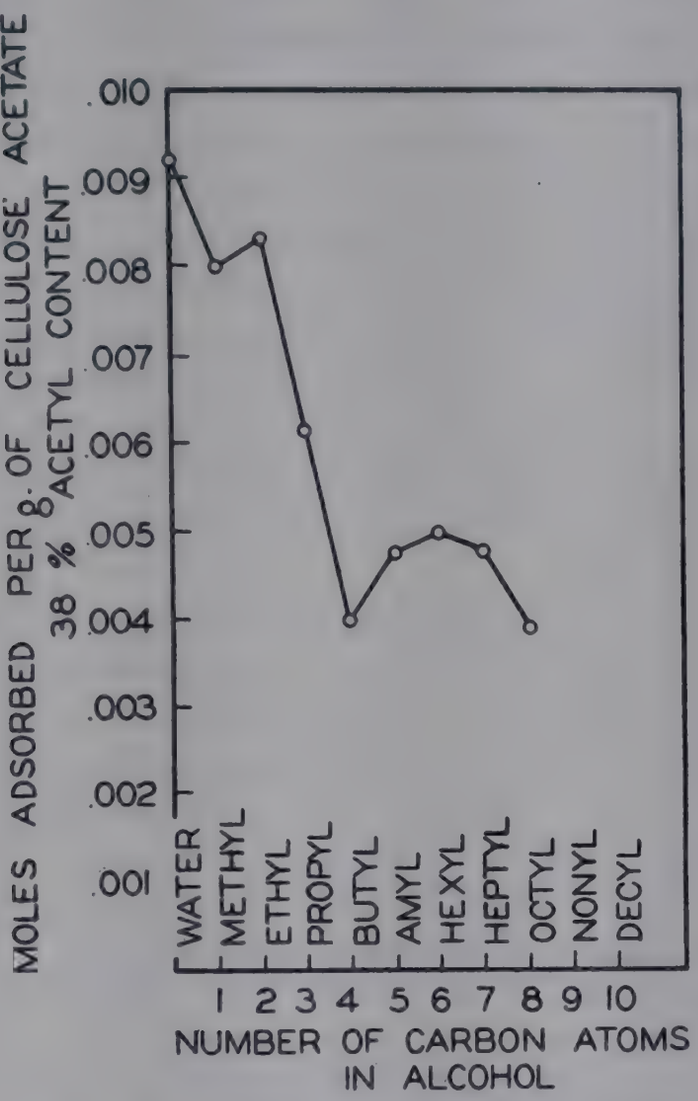

FIG. 80.—ADSORPTION OF VARIOUS ALCOHOLS BY CELLULOSE ACETATE (38% ACETYL CONTENT) AS A FUNCTION OF THE NUMBER OF CARBON ATOMS IN THE ALCOHOL (SHEPPARD AND NEWSOME[26]).

groups seems to yield an increasing contribution to the sorption; and with the triacetate the role of the hydrogen bond is practically eliminated.

(d) *Nonsolvent Water in Fibers*

The water in a swollen fiber shows its reduced activity in a number of ways, including reduced solvent power. The swelling water, in equilib-

rium with an aqueous solution, contains less of the solute than does the surrounding water. Since the exact status of each molecule of the swelling water is unknown, it is customary to assume, when describing an equilibrium partition, that part of the water dissolves no solute at all and the remainder of the water acts as if free. The amount of nonsolvent water is computed under the further assumption that the swelling material does not bind the dissolved reference substance. The validity of this assumption may be checked by determining the apparent amount of nonsolvent water for a number of different concentrations of reference substance. A smaller percentage of the latter should be bound at equilibrium with high concentrations, following the law of mass action. Consequently, in the case of adsorption of the reference substance, the apparent value of nonsolvent water decreases with increasing concentration of the reference substance. If, for a large excess of the reference substance, only a small amount of the latter is bound, then the apparent value of the amount of nonsolvent water with increasing concentration of the reference substance approaches the true value.

The determination is carried out by immersing a swelling substance in a solution, with determination of the concentration of the reference substance in the surrounding liquid before immersion and after attainment of equilibrium. With sodium chloride as reference substance, Schwarzkopf[30] studied water binding by cellulose in alkali hydroxide solutions. Champetier[31] soaked various types of fiber with sodium thiosulfate ($Na_2S_2O_3$), pressed out the solution, and titrated it. The concentration was found to be independent of the extent of expression. Throughout, it was higher than the original concentration. In a further series of tests, pyridine was used as the reference substance.

In all cases, the amount of nonsolvent water bound by native cellulose is about half that bound by mercerized. The amount of nonsolvent water depended only slightly on the relative amount of reference substance, indicating correspondingly slight binding of the latter to the cellulose.

Tankard[32] has recently made use of a refinement of the method of Champetier. He employed pressures so high that cotton, for example, retained only 20 g. of water for each 100 g. of fiber. His results are given in Table 3.

The high values for nonsolvent water recorded for acetate rayon (2.17 acetate residues for each glucose unit) and especially for cellulose tri-

[30] O. Schwarzkopf, *Z. Elektrochem.*, **38**, 353 (1932).

[31] G. Champetier, *Compt. rend.*, **192**, 1593 (1931); **195**, 280 (1932).

[32] J. Tankard, *J. Textile Inst.*, **28**, T263 (1937).

acetate are surprising. Tankard found that the amount of nonsolvent water rises with the degree of acetylation throughout the range of acetyl content.

Using sodium sulfate as the reference substance, Heymann and McKillop[33] found the nonsolvent water of cotton to be 0.12–0.14 g. for each g. of cellulose (1.1–1.2 moles of water for each glucose unit). Sookne and Harris,[34] using trehalose as the reference substance, found 0.12 g. non-

TABLE 3

NONSOLVENT WATER IN CELLULOSE AND CELLULOSE DERIVATIVES (TANKARD[32])

Material	Moles nonsolvent water for each mole $C_6H_{10}O_5$
Cotton	0.49
Mercerized cotton	0.75
Mercerized cotton before drying	0.99
Linen	0.55
Mercerized linen	1.05
Mercerized linen before drying	1.05
Viscose rayon	0.97
Mercerized viscose rayon	1.17
Lilienfeld rayon	1.10
Acetate rayon	2.30
Cellulose monomethylene ether	3.03
Cellulose triacetate	3.00
Hydrocellulose	0.67

solvent water for each g. of cellulose (1.08 moles of water for each glucose unit).

Champetier tried to express the determined ratios between cellulose and nonsolvent water in terms of stoichiometric hydrates. This conception does not agree with the x-ray results, which exclude the entrance of the swelling water within the crystallites, discussed below. The swelling water can be located only on the crystallite surfaces or between them in the amorphous regions, so that no stoichiometric relation can exist. Hess and Schwarzkopf[35] computed, from the x-ray measurements of crystallite size made by Hengstenberg and Mark,[36] that the nonsolvent water found by Champetier is about sufficient for a monofilm over the crystallites. This

[33] E. Heymann and G. C. McKillop, *J. Phys. Chem.*, **45**, 195 (1941).
[34] A. M. Sookne and M. Harris, *Textile Research*, **10**, 405 (1940).
[35] K. Hess and O. Schwarzkopf, *Z. physik. Chem.*, **A163**, 395 (1933).
[36] J. Hengstenberg and H. Mark, *Z. Krist.*, **69**, 271 (1928).

holds both for native and mercerized cellulose fibers. Of course, a sharp distinction of free and nonsolvent water does not correspond to actuality. Rather, a computed value of nonsolvent water is a kind of mean value representing the graduated influence of the cellulose on the whole of the swelling water.

2. Thermodynamics of Sorption

(a) *Heat Evolution Accompanying Sorption*

The take-up of vapor by solids is usually accompanied by the evolution of considerable heat. This heat may readily be measured by adding water

TABLE 4

INTERMEDIATE AND DIFFERENTIAL HEATS OF SWELLING OF COTTON CELLULOSE (ARGUE AND MAASS[37])

Water content, g. per g. cellulose	Integral intermediate heats of swelling, cal. per g. cellulose		Differential heats of swelling, cal. per g. water
	Adsorption	Desorption	
0	10.16	...	...
0.005	9.0	...	232
0.01	8.0	9.29	216
0.02	6.27	7.1	194.5
0.03	4.9	5.32	175.3
0.04	3.78	4.04	159.5
0.05	2.98	3.20	143.6
0.06	2.39	2.64	129.5
0.07	1.99	2.17	116.7
0.08	1.78	...	104.8

to dry fibers in a calorimeter. This procedure gives the integrated value of the heat of swelling. On the other hand, if fibers already containing a definite amount of moisture are used, it is an intermediate heat of swelling which is measured. From values of the latter sort, the differential heat of swelling may be computed. This is defined as the amount of heat evolved during the take-up of 1 g. of water by a very large amount of fiber at a given water content. The heat of *sorption*, which is set free by the take-up of 1 g. of water *vapor*, exceeds the heat of *swelling* by the amount of the heat of *vaporization*. The latter quantity at room temperature is about 600 cal. for each g. of water.

The most exact direct determinations of the heat of swelling of cotton

[37] G. H. Argue and O. Maass, *Can. J. Research*, **12**, 564 (1935).

cellulose are those by Argue and Maass[37] (Table 4). Some hysteresis is observed between the adsorption and desorption values. The values of differential heat of swelling are computed from the data in the adsorption column. The intermediate heats of swelling agree well with previous values of Katz[7] on filter paper. The integrated heat of swelling for cotton was found to be 10.2 cal. for each g. of cellulose. For various preparations of cellulose pulp, Argue and Maass found values between 12.7 and 13.9 cal. The maximum differential heat of swelling evolved by the take-up of 1 g. of water by a large amount of cellulose was calculated. It ranged from 250 to 280 cal. Katz previously calculated about 400 cal. for filter paper.

Besides direct calorimetric measurement, the temperature dependence of sorption affords a possibility of determining the heat effect. Here

$$\Delta H = RT^2 \cdot \frac{d \ln h}{dT} \tag{1}$$

is valid, where ΔH is the heat of sorption of one mole of liquid by a very large amount of fiber, R is the gas constant, T is the absolute temperature, and h is the relative fugacity of the sorbed liquid at the moisture content for which a particular value of ΔH is being computed. Since a measure of relative fugacity is the ratio of the vapor pressure of sorbed water to that of free water at the same temperature, h may be taken equal to the relative humidity of the atmosphere with which the fiber is in equilibrium, and the derivative may be evaluated from a plot of points representing the values of relative humidity which correspond to the same moisture content at a series of temperatures. Equation (1) may then be evaluated under the assumption that h is a function of T alone. This was first done for textile fibers by Shorter.[38] Equation (1) is related to the Kirchhoff and Clausius-Clapeyron expressions for other heat effects.

Neale and Stringfellow[39] carried out the indirect determination of the heat of swelling of cotton cellulose at very low moisture content. They measured the vapor pressure of standard cotton with various moisture contents ranging from 0.012 to 0.16 g. of water for each 100 g. of cellulose in the temperature range of 20 to 80°C. Values of $1/T$ were plotted against the values of the vapor pressure and straight lines were obtained for each moisture content (Fig. 81). Thus, a constant ΔH, the heat of sorption, was found. The numerical value was 15,700 cal. for each mole. The heat of vaporization being 10,500 cal. for each mole, the heat of swelling

[38] S. A. Shorter, *J. Textile Inst.*, **15**, T328 (1924).

[39] S. M. Neale and W. A. Stringfellow, *Trans. Faraday Soc.*, **37**, 525 (1941).

found was 5200 cal. for each mole of water or 280 cal. for each g. of water. This value agrees very well with the direct determination of Argue and Maass.

Hoffmann[29] determined by calorimetric measurements the heat of swelling of cellulose triacetate in organic solvents and found for trichloroethylene 11.4 cal., for benzyl alcohol 8.2 cal., and for benzyl chloride 8.1 cal. for each g. of cellulose acetate. The maximum differential heat of swelling

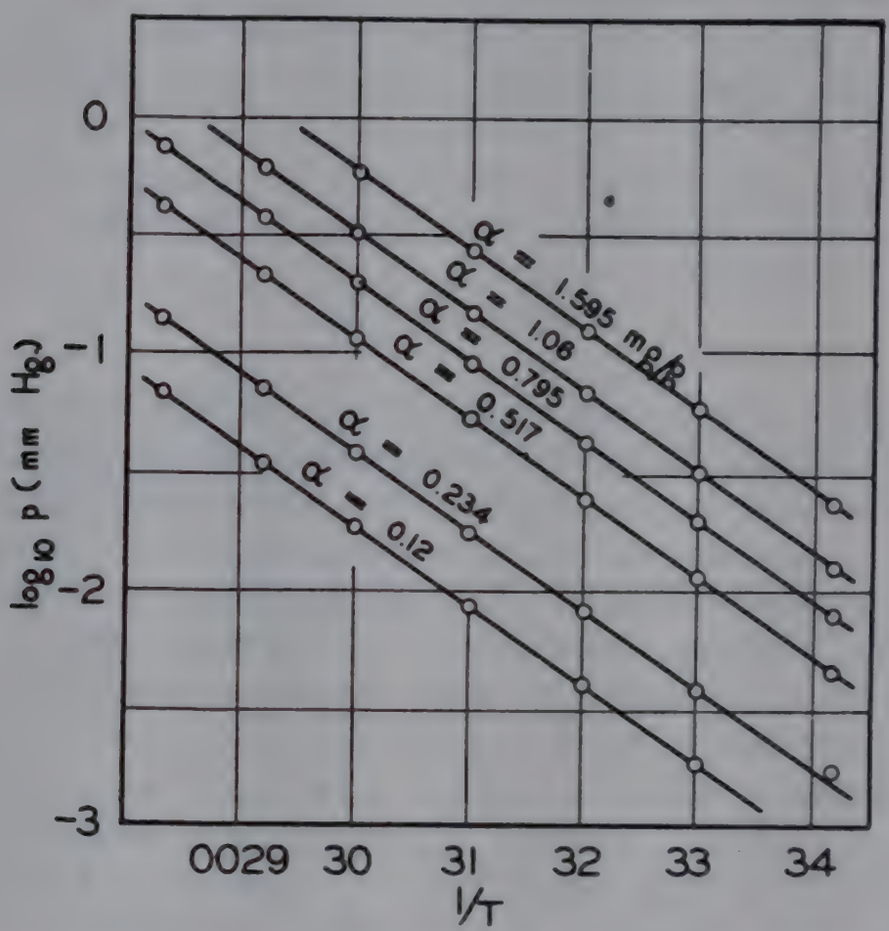

FIG. 81.—SORPTION ISOSTERES OF COTTON AT VARIOUS MOISTURE CONTENTS (NEALE AND STRINGFELLOW[39]).

α = mg. water per g. cotton.

was only 60 to 160 cal. for each g. of solvent, which is much lower than the values found for water.

Sheppard and Newsome[40] determined the heat of sorption of cellulose acetate from the temperature dependence of the sorption and also by the calorimetric method. The maximum heat of swelling was found to be about 240 cal. for each g. of water. This value is in the same range as those for cotton and wool. The same authors determined the integral

[40] S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.*, 37, 389 (1933).

heat of swelling of cellulose acetate with water and organic solvents. In general, the heats of swelling were largest for cases of largest take-up.

Morrison, Campbell, and Maass[41] determined the integral heat of swelling of standard cellulose with various alcohols and their aqueous solutions. Water itself gave about 10 cal. for each g. of fiber, while methanol gave 7.0, and the rest of the alcohols gave less than 1.0 cal. per g. The high value for methanol is noteworthy. For methanol-water mixtures, the values are a linear function of the water content. For the other alcohols, the heats drop off linearly with increase in the alcohol content to 80 mole per cent, but more sharply thereafter. These relations are explicable on the assumption of preferential sorption of water by cellulose from the solution. Further values for the heat of swelling are to be found below.

(*b*) *Free Energy and Entropy of Swelling*

From the sorption isotherms, as Katz[7] has shown, the work content change accompanying sorption may readily be computed. The work content change of swelling is given by

$$\Delta A = RT \ln h \tag{2}$$

where h is the relative humidity with which the sample is in equilibrium, and ΔA is the maximum work which may be performed by the reversible addition of one mole of water to a large amount of sorbent. For 1 g. instead of one mole, at room temperature, and using common logarithms,

$$\Delta A = 69 \log h \tag{3}$$

This maximum work, in calories, may be performed in an ideal experiment in which one mole of liquid is isothermally added to a large mass of fiber, assumed compressed against a permeable membrane by a piston. To the latter is applied force enough so that an infinitesimally slight increase in pressure will result in liquid being squeezed from the fiber. Under these reversible conditions, the pressure on the piston head will equal the swelling pressure, and will be given by

$$P = -2935 \log h, \tag{4}$$

where P is in atmospheres. For the take-up of 1 g. of water, assuming no contraction, a piston of q cm.^{2} area will be driven back $1/q$ cm., and the work done against the balancing force will be the ΔA given by Equation (3).

From a theoretical standpoint, it is interesting to compare the heat and the free energy of swelling and, by applying the second law of thermo-

[41] J. L. Morrison, W. B. Campbell, and O. Maass, *Can. J. Research*, **15B**, 447 (1937).

dynamics, to calculate the entropy change. For constant pressure and temperature, we can write

$$\Delta F = \Delta H - T\Delta S \tag{5}$$

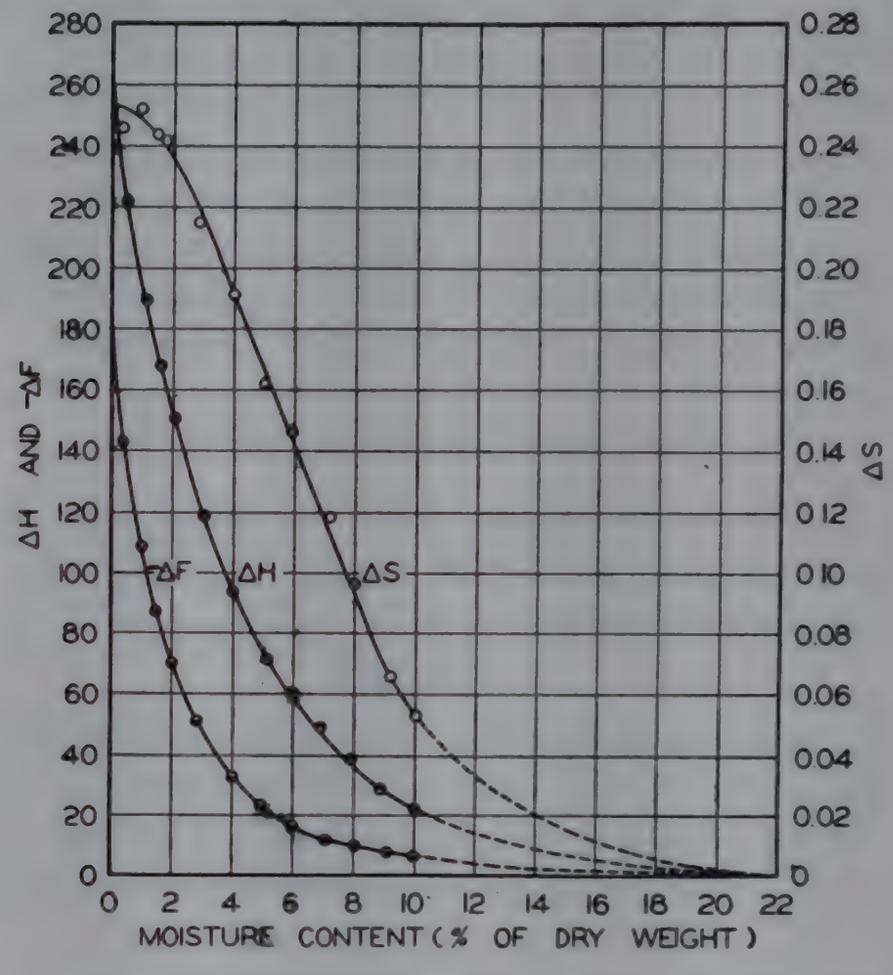

FIG. 82.—DIFFERENTIAL HEAT OF SWELLING, AND FREE ENERGY AND ENTROPY CHANGES WITH MOISTURE CONTENT AT 50°C. FOR SODA-BOILED COTTON (STAMM AND LOUGHBOROUGH[42]).

Calculated from the data of Urquhart and Williams.

wherein ΔF denotes the change of free energy and ΔS the change of the entropy. On the other hand,

$$\Delta F = \Delta A + p\Delta V \tag{6}$$

wherein p denotes the pressure and ΔV the volume change. For the swelling process, $p\Delta V$ can be neglected as compared with the work content change, and, hence, the free energy can be substituted for the work content.

Stamm and Loughborough,[42] using Equations (1) and (2), computed

[42] A. J. Stamm and W. K. Loughborough, *J. Phys. Chem.*, **39**, 121 (1935).

differential heats of swelling and free energy changes for cotton from the data of Urquhart and Williams.[3] The heats of swelling were calculated from the 40 and 60°C. isotherms. The 50°C. isotherm was used to determine the change in the free energy. The entropy change was then found from Equation (5). Figure 82 shows that the change of heat content is much greater than the change in free energy. Indeed, the latter is a rather small fraction of the former in the range of medium and high relative humidity. These values of the differential heats of swelling are lower than

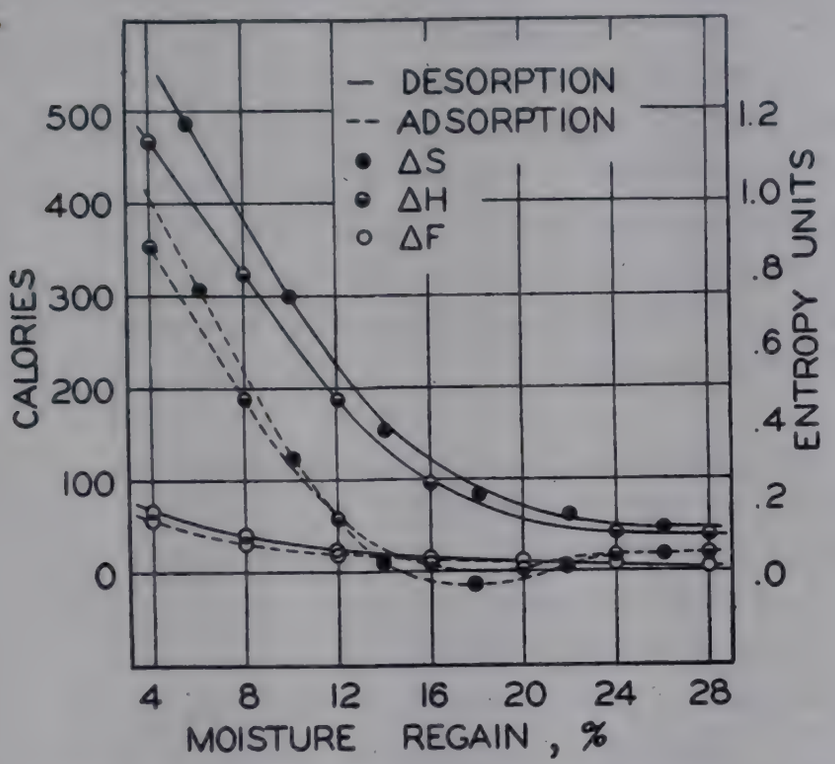

FIG. 83.—DIFFERENTIAL HEAT OF SWELLING AND FREE ENERGY AND ENTROPY CHANGES OF CELLOPHANE AS A FUNCTION OF MOISTURE CONTENT AT 30.4°C. (SIMRIL AND SMITH[22]).

those measured directly by Argue and Maass (Table 4). However, the value for zero moisture content, 280 cal., agrees well with the value of Argue and Maass.

Houtz and McLean[24] computed, from their previously mentioned data for paper, the differential heats of swelling at high temperatures. These data allow close determination of the maximum heat of swelling. This, at 100°C., is 354 cal. for each g. of water, and therefore is only slightly above those determined by Argue and Maass and computed by Stamm and Loughborough. The value for the differential entropy at 0.5% RH, namely 0.22 cal. for each degree for each g. of water, is also close to the

value of Stamm and Loughborough. The value of $T\Delta S$ for each g. of water, near zero moisture content, is about -82 cal. in both cases.

Simril and Smith[22] computed the corresponding values for cellophane. On the basis of the sorption isotherms for various temperatures which were previously mentioned, they plotted log p (p = vapor pressure) against $1/T$. In contrast to the finding of Neale and Stringfellow on cotton, the isosteres so obtained are not straight. Consequently, the calculated values of ΔH are not constant for a given moisture content but decrease with increasing temperature especially rapidly at low moisture contents. Nevertheless it could be assumed that over small temperature ranges Equation (1) may be employed without gross error. On this assumption, ΔH values for various moisture contents were calculated from the isotherms for 24.8 and 35.9°C. The resulting curves for the heat content changes of the adsorption and the desorption at 30.4°C. are shown in Figure 83. The values are much higher than the corresponding values for cotton cellulose. Consequently, the $T\Delta S$ values are also much higher. The values for desorption are considerably higher than those for adsorption.

The thermodynamic data at hand are an adequate basis for discussing the determining factor in the take-up of water by cellulose. A distinction can be made between processes which are caused by the kinetic movement of the molecules and between processes which are caused by intermolecular attraction. In the first case, the change in heat content is vanishingly small, as in the case of the expansion of an ideal gas or the dilution of an ideal solution. The large heat content change of the swelling actually observed proves that in the swelling process the molecular interaction figures prominently.

Several attempts have been made to explain the swelling as an osmotic phenomenon. Haller[43] believed the thermal vibrational movement of the long fiber molecules responsible for the swelling. Staudinger[44] suggested that the rotational movement of giant rod-shaped molecules causes the swelling of the high-polymeric substances. These explanations, however, can only fit cases in which the free energy change exceeds the heat content change. Consequently, with fibers they can be applied, if at all, only to the range of 90 to 100% RH. For the remaining greater portion of the relative humidity range, it is certain that the take-up occurs against

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[43] W. Haller, *Kolloid-Z.*, 49, 74 (1929).

[44] H. Staudinger, *Die hochmolekularen organischen Verbindungen*. J. Springer, Berlin, 1932.

the effect of the thermal movement. Therefore, the explanation must account for the decrease of the entropy by the swelling process. Katz[7] suggested that a high organization of the sorbed water causes the reduction of the entropy. The $T\Delta S$ value at zero moisture content is, in fact, as found by Stamm and Loughborough[42] and by Houtz and McLean,[24] roughly equal to the latent heat of fusion of water, implying that the first amount of sorbed water has a degree of orientation and association comparable to that of ice.

The intermolecular forces which cause the swelling can be considered identical in nature with those effective in solvation, which are known to be of specific nature. The behavior observed in each case of sorption is characteristic of the sorbent and the sorbed material. An example of this was given above in the dependence of water take-up by cellulose acetate on the degree of esterification. Heat of swelling, therefore, has a meaning analogous to heat of solution. The latter, in the case of a solid solute, is the heat of solvation minus the cohesion energy (lattic energy), since the lattice forces must be overcome during the process of solution. The same relations hold in swelling. The water or other liquid forces itself between the portions (crystallites or molecules) of the swelling body. In the dry state, these units are held together by forces of large magnitude, but these cohesion forces are overcome by the solvation forces. The observed heat of swelling is the result of an equilibration of two effects.

Hydrogen bonding indubitably plays an essential role in the sorption of water by fibers. The water molecules interact with the hydroxyls of cellulose. In the case of sorption, there is a replacement of hydrogen bonds between fiber and fiber molecules by bonds between water and fiber molecules. In the case of swelling, there is a replacement of hydrogen bonds between water and water, and between cellulose and cellulose molecules, by bonds between water and cellulose molecules.

The energy of hydrogen bonds averages roughly 5000 cal. for each mole. This corresponds approximately to 280 cal. for each g. of water. It has been shown that the maximum differential heat of swelling of cellulose is about 300 cal. for each g. of water. However, if the picture which was just put forward is correct, the swelling process causes a decrease rather than an increase of the number of hydrogen bonds. Consequently, the heat of swelling cannot be identified with the energy of newly formed hydrogen bonds but with the surplus of the energy of newly formed bonds over the energy of disrupted bonds.

Neale and Stringfellow[39] in pointing out the unexpected magnitude of the heat of swelling suggest that in the stage of primary sorption each water

molecule is directly linked to a pair of suitably placed cellulose hydroxyl groups. If this conception is correct, the sorption does not represent a replacement of the hydrogen bonds between the hydroxyl groups of the cellulose but the interaction of water with previously unsaturated hydroxyl groups of the cellulose, at least in the range of low moisture content. However, as Neale and Stringfellow state, even in this case it is necessary to assume that the new hydrogen bond has a higher energy than that of the hydrogen bonds of water and of alcohol. It should have the energy of the hydrogen bond of acetic acid.

It may be pointed out that the forces of the hydrogen bond are only a part of the van der Waals' forces which cause the intermolecular attraction. The mixing of ethanol or glycol with water, for example, generates a considerable amount of heat and produces contraction although it results in a replacement of the water-water and alcohol-alcohol interaction by water-alcohol interaction. Until it is known by what molecular mechanism the heat effect is produced in this case, it is futile to speculate on the origin of the heat effect of the swelling of cellulose.

The behavior of fibers is somewhat different from that of porous bodies such as charcoal or silica gel. The latter have the ability to take up large amounts of vapor without marked volume change. In this case, capillary condensation is doubtless important, in addition to adsorption on solid surfaces. Since it is occasionally assumed that capillary condensation is important in the take-up of vapors by fibers, and, indeed, that it is the exclusive mechanism, a brief discussion is in order.

Capillary condensation is the phenomenon in which vapor is condensed to liquid in narrow pores at pressures below the saturation pressure. The cause is the relatively large effect of surface tension in reducing vapor pressure at the sharply concave surface of a liquid in a small capillary. For every pore diameter and liquid, there is a definite pressure at which condensation occurs (Table 5).

TABLE 5

RELATIVE HUMIDITY (RH) AT WHICH CONDENSATION OF WATER OCCURS IN CAPILLARIES OF DIFFERENT RADII (r)

r	(Å.)	100	50	30	20	10
RH	(%)	90.3	81.6	71.2	60.1	36.2

Below 36% RH the pore size for condensation at one atmosphere external pressure is so small that every water molecule within it must be strongly influenced by the pore surface. Only above this diameter, when the water

molecules are small relative to the capillary width, is it possible to speak of condensation in the usual sense. Observation shows that water take-up by fibers leads to an increase in the fiber diameter; whereas condensation in capillaries should, if anything, produce a slight shrinkage of the sorbing body by pulling the walls closer together. Further, the heat effect of capillary condensation should be simply a heat of vaporization, but the observed heat effect is much larger. Finally, the specific nature of sorption for various combinations of fiber and vapor is contrary to the expected behavior of preformed holes. The latter would presumably take up approximately equal amounts of all vapors, with perhaps small variations caused by differences of surface tension and normal vapor pressure. The observed take-ups correlate badly with those expected on such an assumption. It may be stated that condensation of water in preformed spaces within dry fibers can scarcely be expected to contribute more than 0.02 to 0.03 g. of water for each g. of fiber to the total sorption, since the observed density of fibers agrees well with that computed from microscopic cross-section measurements and x-ray determinations of the unit cell. Undoubtedly, however, the state of sorbed water is closer to liquid or even solid than to gaseous.

Consequently it is justified to consider in the thermodynamical treatment the change of the heat content, the free energy, and the entropy in the sorption process relative to liquid rather than to gaseous water.

Peirce,[45] and with some modifications Sheppard and Newsome,[15] suggested a two-phase theory of sorption. The sorption isotherm is split by this treatment into two components, one representing the moisture held by capillary forces and the other representing the moisture held by chemical interaction. The first curve has approximately the form of a Langmuir isotherm converging toward a saturation value which for cotton is about 0.05 g. of water for each g. of cellulose. The remaining portion of the sorbed water is plotted on the second curve which is concave upward. From this standpoint the differential heat and the differential contraction could be calculated for the primary sorption as roughly constant. On the other hand, the take-up by capillary forces would proceed without appreciable heat effect and contraction above that of the ordinary condensation. Such a treatment assists in the understanding of the sorption phenomenon, if the fact is not overlooked that the two processes, primary sorption and capillary condensation, occur simultaneously and

[45] F. T. Peirce, *J. Textile Inst.*, **20**, T133 (1929).

inseparably. Stamm[46] points out the difficulty for the two-phase theory which lies in the fact that many peculiarities of the sorption, for example, the S-shaped isotherm, the dependence of the heat, and the contraction, are similarly exhibited by the water take-up of sulfuric acid. In this case, however, the assumption of a capillary condensation is out of question.

3. Dimensional Changes of Fibers Accompanying Sorption

(*a*) *Changes in Actual Fiber Dimensions*

Measurement of the water take-up of fibers by following the dimensional changes is a process of interest from several viewpoints. For one thing, the increase of length is only a fraction of the increase in width. This large anisotropy of swelling is characteristic of fiber structure. Further, it is interesting to determine whether the moisture taken up produces an increase equal to its own volume in the size of the fiber. This question is related to the problem of whether the sorbed water merely fills pores already present though invisible, or actually forces its way between parts of the fiber, with increase of the distance between the parts. Dimensional changes of fibers are technically important because of their relation to the shrinkage of fabrics.

Volume change of fibers may be studied microscopically in two ways: it is possible to watch the change of width from the side of the whole fiber, or to watch the change of a thin cross section. Because of the irregular form of the cross section, the latter method is the more exact. This is particularly true for cotton, which, when dry, has the form of a flat band and frequently displays an empty lumen in the center of the fiber. Change in length may be followed macroscopically. However, because of the difficulty of measuring the length without applying tension and because of the smallness of the effect, the method is inexact. In all microscopic measurements of fiber swelling, it is necessary to make a large number of single determinations and to treat them statistically. Even when this condition is fulfilled, systematic errors are here large enough so that no great precision can be claimed for the results.

It was shown long ago that the maximum change of length of natural cellulose fibers on adsorption of water is less than 1%. It follows that nearly the whole of the volume change is that of the cross section.

Clayton and Peirce[47] observed the dimensional changes accompanying

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[46] A. J. Stamm, *Colloid Chemistry of Cellulosic Material.* U. S. Dept. Agr., Washington, 1936.

[47] F. H. Clayton and F. T. Peirce, *J. Textile Inst.*, **20**, T315 (1929).

water sorption by thirteen kier-boiled and eight mercerized cotton fibers. The mean increase of diameter on passing from the dry state to saturation with water vapor was 15% ± 2%. Allowing for a slight increase in length, the computed volume change was, therefore, 34%. Since the density of cotton is about 1.6, the weight increase corresponding to this swelling was about 22%. An exact comparison of this result with the direct measure-

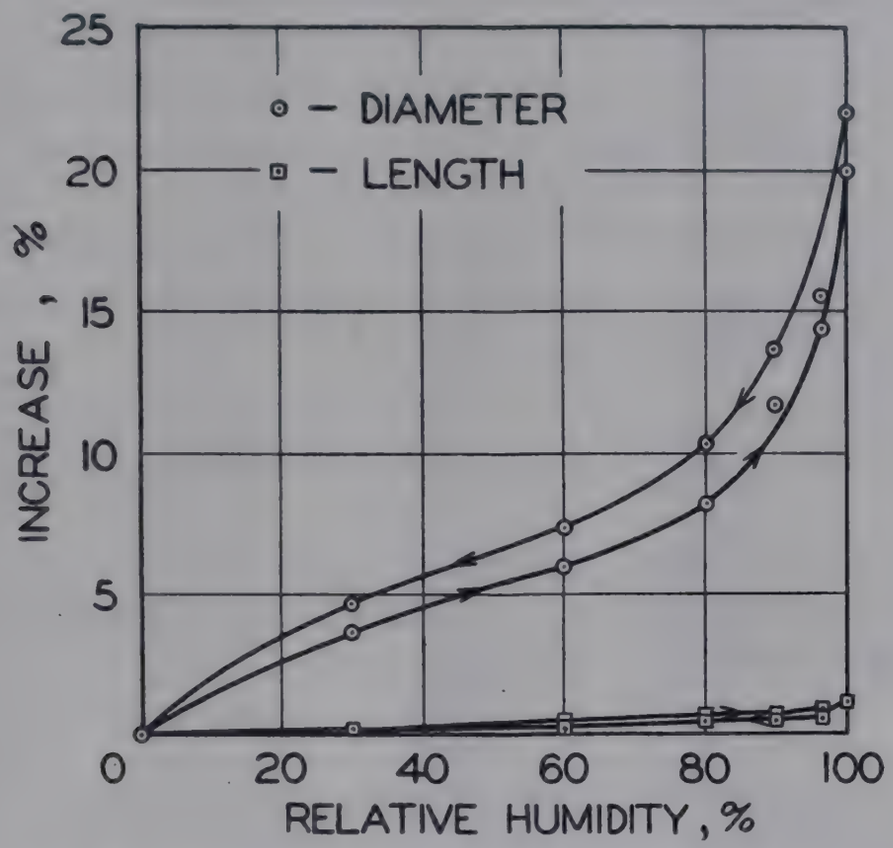

FIG. 84.—DIMENSIONAL CHANGES OF COTTON HAIR DURING SORPTION OF WATER (COLLINS[48]).

ment of the take-up is prevented by the difficulty mentioned previously: the sorption isotherm becomes nearly parallel to the ordinate axis in the region of high relative humidities. A rough agreement may be claimed. The volume change for the mercerized cotton appeared to be slightly less than that for the kier-boiled.

Collins[48] investigated cotton fibers over the whole humidity range. Figure 84 contains the mean values of his observations on seven fibers for both adsorption and desorption. It is apparent from these results that the phenomenon of hysteresis is also shown by the dimensional changes. The values of Collins are in approximate agreement with those of Urquhart

[48] G. E. Collins, *J. Textile Inst.*, **21**, T311 (1930); **30**, P46 (1939).

and Williams, if the specific volume of the absorbed water is between 0.8 and 1.0. The reality of the volume contraction is a subject for further discussion (see below).

Table 6 contains some results of A. Herzog[49] on artificial fibers. The values here are averages of many single determinations carried out on microscopic preparations in the dry and moistened states. One can recognize here the small swelling of the acetate rayon which was also shown by the sorption isotherm.

TABLE 6

SORPTION OF WATER BY ARTIFICIAL FIBERS (HERZOG[49])
Per cent increases on swelling

Fiber	Length, %	Cross section, %	Volume, %
Cuprammonium rayon	3.65	61.8	67.8
Nitrate rayon	0.77	45.2	46.4
Viscose rayon	4.80	65.9	73.9
Acetate rayon	0.14	5.7	6.0

Lawrie[50] found for artificial fibers the values given in Table 7. In this table, dimensional changes were computed relative to the dimensions of the fibers at medium humidities (60 to 70% RH).

TABLE 7

SORPTION OF WATER BY ARTIFICIAL FIBERS (LAWRIE[50])
Average per cent increases of cross section on swelling

Viscose rayon	35%	Bemberg (cuprammonium)	41%
Vistra	52%	Celanese (acetate)	9%
Celta	25%	Rhodiaseta (acetate)	14%
Tubize nitrate rayon	30%	Courtaulds (acetate)	11%
Other nitrate rayons	33%	Lustron (triacetate)	3%
Brysilka (cuprammonium)	53%	Other triacetates	2%

(*b*) *Volume Contraction during Swelling*

The swelling of high polymers is frequently accompanied by a contraction in the total volume of the system. The volume of dry fibers plus that of liquid taken up is more than the volume of the resulting swollen fibers.

[49] A. Herzog, *Die mikroskopische Untersuchung der Seide und der Kunstseide*. J. Springer, Berlin, 1929.

[50] L. G. Lawrie, *J. Soc. Dyers Colourists*, **44**, 73 (1928).

This effect is encountered in the measurement of the density or specific volume of fibers by the liquid displacement method: the amount of fluid displaced by a gram of fibers is dependent on the nature of the fluid. This dependence may be caused by the differences in the ease with which various liquids penetrate the capillaries, or to the differences in the volume contraction under the influence of the mutual attraction forces of the fibers and the swelling medium.

Davidson[51] measured the specific volume of cotton with three different media: gaseous helium, liquid toluene, and liquid water (Table 8). It is a safe assumption that helium is not bound in significant amount to cotton.

TABLE 8

APPARENT SPECIFIC VOLUMES (CC. PER G.) OF CELLULOSE FIBERS AT 20°C. (DAVIDSON[51])

Fiber	Medium		
	Helium	Water	Toluene
American Upland, soda-boiled	0.638	0.6213	0.645
American Upland, mercerized	0.645	0.6224	0.651
Sea Island, mercerized	0.647	0.6243	0.653
Sea Island, soda-boiled	0.642	0.6235	0.646
Sakel, soda-boiled	0.640	0.6226	0.645
Sakel, mercerized	0.645	0.6234	0.651
Viscose rayon	0.646	0.6217	0.652
Cuprammonium rayon	0.653	0.6248	0.657
Nitrate rayon	0.648	0.6192	0.654

The only possible interaction is that provided by van der Waals' forces, which are smaller for helium than for any other substance. Even the powerful sorbent animal charcoal scarcely takes up helium. Thus, no contraction is anticipated. Further, because of its very small molecular volume, helium may be expected to penetrate the finest pores and capillaries of the fiber. It follows that the helium values may be taken as the true specific volumes. The values found with toluene and other organic liquids are higher, presumably because the larger molecules of these liquids cannot work into all the pores and channels. The lower specific volumes found with water may be explained by assuming that the interaction of water and cellulose molecule is greater than that of water molecules with themselves; thus, contraction of the total volume ensues.

The observations of Brimley[25] of the sorption of various vapors by cotton

[51] G. F. Davidson, *J. Textile Inst.*, **18**, T175, T275 (1927).

show that the organic liquids used by Davidson as embedding media are indeed taken up by the fiber only to a minute extent.

The contraction accompanying water take-up by cellulose may be calculated from the difference between the apparent specific volume in water and in helium (Table 9). Values of the maximum water take-up, computed or estimated from the measurements of Urquhart and his collaborators, are also included. The last column contains the apparent specific volume of the sorbed water calculated from these data. The contraction of total volume for maximum water take-up is about 2 to 3 cc. for each 100 g. of cellulose. The density of the sorbed water thus appears to be

TABLE 9

CONTRACTION ON WATER TAKE-UP BY CELLULOSE (DAVIDSON[51])

Fiber	Contraction, cc. per g. cellulose	Maximum take-up, g. per g. cellulose	Sp. vol. of sorbed water, cc. per g.
American Upland, kier-boiled	0.017	0.23	0.929
American Upland, mercerized	0.023	0.36	0.939
Sea Island, kier-boiled	0.019	0.23	0.921
Sea Island, mercerized	0.023	0.32	0.931
Sakellaridis, kier-boiled	0.018	0.23	0.926
Sakellaridis, mercerized	0.022	0.30	0.930
Viscose rayon	0.025	0.45	0.948
Cuprammonium rayon	0.028	0.43	0.936
Nitrate rayon	0.029	0.44	0.936

about 5 to 7% higher than that of free water. Davidson computed the pressure requisite to compress water to this extent, finding values of 1500 to 2000 kg./cm.^{2}

It is noteworthy that, as Davidson's results show, the higher sorption of mercerized cotton and regenerated cellulose is associated with higher values of total contraction. The specific volume of water sorbed by these fibers, however, appears to be 1 to 2% higher than that sorbed by kier-boiled cotton.

There is considerable doubt as to the reality of the contraction. The question remains open as to whether submolecular or supermolecular interstices disappear or are reduced when water is taken up. Only the former case can correctly be denoted as contraction. Weltzien[52] mentioned the possibility that certain spaces within the fibers may be reached by

[52] W. Weltzien, *Chemische und physikalische Technologie der Kunstseide.* Akademische Verlagsgesellschaft m.b.H., Leipzig, 1929.

water after swelling, though they may be barred to helium gas in the dry state. In this case, the assumption of contraction becomes void. This possibility cannot be excluded, particularly since (as shown below) the permeability for gases of water-swollen cellulose is considerably higher than that of dry cellulose. A direct experimental distinction requires the determination of the true value of the density by an independent method. With a crystalline cellulose preparation, the density may be determined by x-ray methods. For native cellulose, the true value thus found for the

TABLE 10

CONTRACTION ON WATER TAKE-UP BY CELLULOSE (FILBY AND MAASS[53])

Water take-up, g. per g. cellulose	Apparent volume of sorbed water, cc.	Contraction, cc. per g. cellulose	Density of sorbed water
0.0320	0.0123	0.0197	2.60
0.0625	0.0255	0.0370	2.45
0.1090	0.0723	0.0367	1.50
0.1578	0.1245	0.0333	1.26

specific volume is 0.629 (for mercerized cellulose 0.633), which indicates the reality of the contraction. Of course, there remains the possibility that the assumed value of the contraction is somewhat too high, as the specific volume which was found with helium and which was the basis for the calculation for the contraction was higher than the x-ray value. On the other hand, cotton contains amorphous material too, and it is to be expected that the amorphous material has a higher specific volume than the crystalline.

Filby and Maass[53] likewise employed the gas displacement method, using helium, to ascertain the specific volume of Kodak rag cellulose which had been kier-boiled. The result, in excellent agreement with that of Davidson, was 0.640 ± 0.001 cc. for each g. With the same method, they determined the specific gravity of cellulose samples which had sorbed various amounts of water. The results are given in Table 10 and in Figure 85.

From these results, it would appear that only the first portion of the sorbed water undergoes contraction and that the total contraction is somewhat higher than that found by Davidson, being about 0.037 cc. for each g. of cellulose.

However, these results could not be confirmed by Stamm and Seborg

[53] E. Filby and O. Maass, *Can. J. Research*, **7**, 162 (1932).

who determined the contraction of the sorbed water, using benzene as the pycnometric liquid and samples of cotton of various moisture contents.[54] Figure 86 contains the data so obtained, and also the values of the differential contraction; that is, the reduction of volume consequent upon the sorption of 1 g. of water by a large amount of cotton at a given relative humidity. The total value of the integral contraction was found to be 0.017 cc., in fair agreement with the results of Davidson.

For the apparent density of cellulose, Stamm and Hansen[55] obtained values closely equivalent to those of Davidson (Table 8). They used these values and those of Stamm and Seborg[54] to compute the pressure which

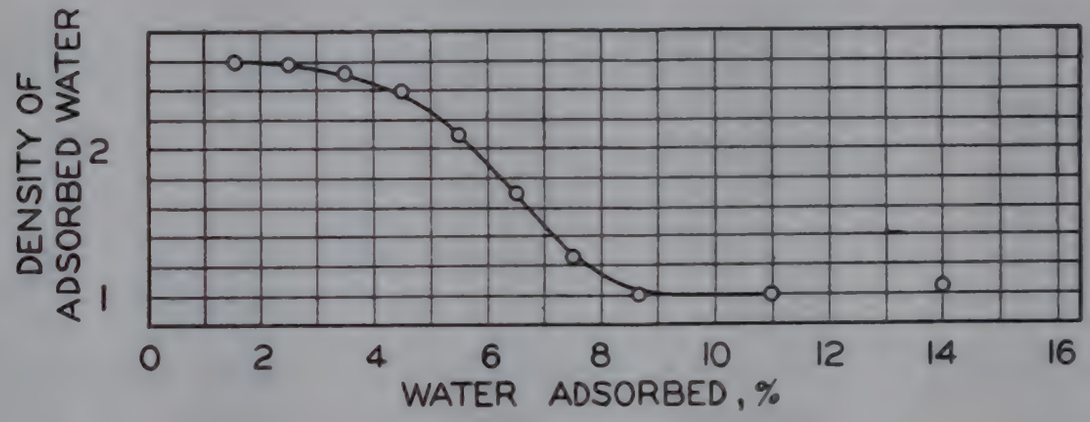

FIG. 85.—APPARENT DENSITY OF WATER ADSORBED BY COTTON AS A FUNCTION OF MOISTURE CONTENT (DIFFERENTIAL VALUES) (FILBY AND MAASS[53]).

would be needed to compress the sorbed water far enough to give the observed contraction. In this way they found that the initial value of the differential contraction corresponds to a pressure of 14,000 atm. Pure water is itself subjected to 12,500 atm. by its intramolecular cohesion forces. The 14,000 atm. must be added to this, so that the total internal pressure of the first water sorbed is 26,500 atm. For the total sorbed water and, correspondingly, the total contraction, the internal pressure is increased 17% (to 14,700 atm.) for cotton and 8% (to 13,500 atm.) for sulfite pulp.

Stamm and Hansen pointed out that, as was already observed by Katz,[7] there is a fairly constant ratio between the heat of mixing and the change of internal pressure produced by diluting with water such materials as glycerol, glycol, mineral acids, alkali hydroxides, etc. For cellulose, it is

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[54] A. J. Stamm and R. M. Seborg, *J. Phys. Chem.*, **39**, 133 (1935).

[55] A. J. Stamm and L. A. Hansen, *J. Phys. Chem.*, **41**, 1007 (1937).

possible to compute the heat of swelling (see below) instead of a heat of mixing. Stamm and Hansen found the same constant ratio between the heat of swelling of cellulose and its internal pressure. This is at present the best support for the assumption that the values of contraction found from the densities in helium are in the main correct.

Macmillan[27] determined the specific gravity of jute by the pycnometric method. A high value was found with acetone, but this is concordant

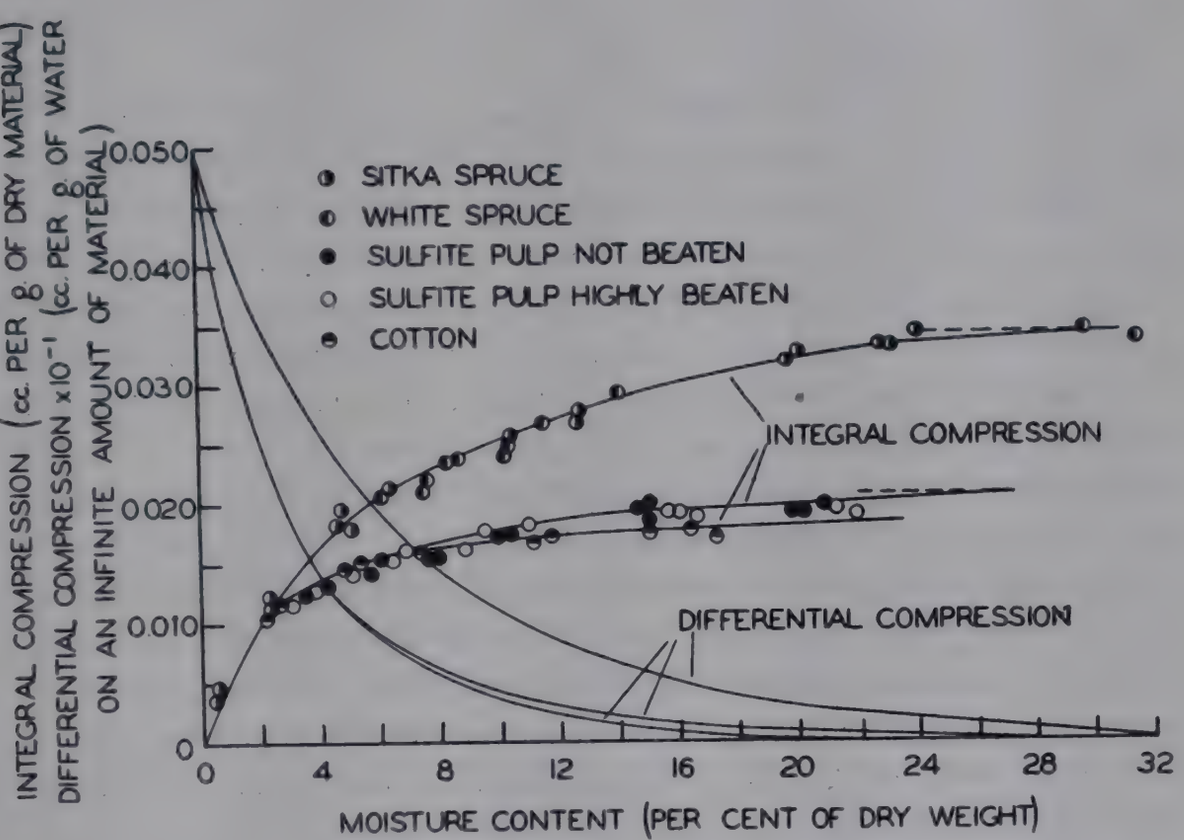

FIG. 86.—APPARENT CONTRACTION OF WATER AS A FUNCTION OF THE MOISTURE CONTENT OF VARIOUS CELLULOSIC MATERIALS (STAMM AND SEBORG[54]).

with the relatively strong sorption of this solvent by jute (cf. Table 1). The benzene used may not have been quite anhydrous. Macmillan assumed that 1.436 should be taken as the true density. Then the total contraction on take-up of water becomes 9 cc. for each 100 cc. of fiber, a rather high value, even considering the high value (54 cc. of water for each 100 cc. of jute) of maximum water take-up.

(c) *Intermicellar Nature and Anisotropy of Swelling*

There are two possibilities for the mode of distribution of the molecules of a swelling liquid; namely, homogeneous distribution with solid solution

or solvate formation, or inhomogeneous distribution with the formation of liquid-filled channels.

The botanist Nägeli[56] considered, about a century ago, that the second possibility is the one which holds for the swelling of vegetable fibers. He envisioned molecular bundles, which he named micelles, which could be separated from each other on contact with a swelling medium without being themselves penetrated. In this terminology, the first possibility above may be called intermolecular, the second intermicellar, swelling. If the existence of micelles is acknowledged, the first mode may also be characterized as intramicellar swelling.

In many cases, the x-ray method furnishes ready confirmation of Nägeli's formulation. Katz[57] was the first to show that the spacings of the cellulose x-ray diagram are entirely unchanged by swelling in pure water. This holds for mercerized as well as for native cellulose, and even for rayon. It follows that the water certainly does not penetrate the crystallites. Should it do so, a shift or vanishing of certain interferences would be detectable. In Nägeli's terminology, therefore, swelling in pure water is an intermicellar rather than an intramicellar process.

Bonhoeffer,[58] as well as Champetier and Viallard,[59] pointed out a noteworthy property of cellulose swelled by water. They showed that treatment of cellulose with heavy water replaced, by deuterium, three hydrogen atoms in every glucose residue. Apparently, the hydroxyl hydrogens are exchanged throughout the entire fiber substance. This appears to contradict the concept of purely intercrystalline swelling. However, according to x-ray measurements of crystallite size, about half of the glucose residues lie on the crystallite surfaces, and the assumption of a certain mobility of the hydroxyl groups in the crystallites is adequate to account for the exchange. Bonhoeffer found that the exchange with filter paper is complete in a few days at 100°C. Champetier and Viallard accomplished the exchange with filter paper in 13 hours at 100°C., and in 24 hours at 30°C. With cotton linters, 36 hours at 30°C. is required.

Anisotropy of swelling is a fact of great importance in the structure of fibers. Full swelling of natural fibers produces only slight changes of length. For jute, the increase is 0.37%; for cotton, 1.1%; for wool, 1.2%; and for silk, 1.3 to 1.7%. On the other hand, the increase of diameter is

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[56] C. Nägeli, *Die Micellartheorie*. Ostwald's *Klassiker* No. **227**, Leipzig, 1928.

[57] J. R. Katz, *Physik. Z.*, **25**, 321 (1924).

[58] K. F. Bonhoeffer, *Z. Elektrochem.*, **40**, 469 (1934).

[59] G. Champetier and R. Viallard, *Compt. rend.*, **205**, 1387 (1937).

15 to 20%, or more than tenfold the length increase. Regenerated cellulose fibers expand lengthwise about 5%, crosswise about 30 to 40%.

Nägeli assumed an extended form for the micelles, with the long axes paralleling the fiber axis. According to this picture, an increase in intermicellar separation (swelling) would cause an increase of width greater than the lengthening; since vectors normal to the micellar surfaces would mostly be normal also to the fiber axis. The anisotropy of swelling might be a measure of the orientation and axial ratio of the micelles. However, it is obvious that the phenomenon of anisotropy does not necessitate the assumption of intermicellar swelling. Because the primary valence chains themselves are much greater in length than in width, orientation of the chains parallel to the fiber axis would also produce anisotropy of swelling if the water were adsorbed on the surface of the fiber molecules. Only the advent of further experimental methods, particularly x-ray procedures, made possible a distinction in favor of intermicellar swelling.

The distinction between the intramicellar and intermicellar swelling is based on a schematic conception of polycrystalline texture. The x-ray diagrams show with certainty only that the water does not uniformly penetrate the material of the fiber, but preferentially enters the amorphous regions. It is to be expected that swelling water will prefer the intercrystalline, disturbed regions, since it must overcome the cohesion forces of the fiber material. Amorphous (fluid or disordered) substances show weaker cohesion than the same substances regularly arranged in space lattices.

As mentioned above, the anisotropy of swelling can be regarded as a measure for the orientation and the axial ratio of the structural elements (molecules, micelles, crystallites), the surface of which is adsorbing the water. Hermans[60] investigated the relationship between orientation and anisotropy of swelling. He prepared completely isotropic cellulose fibers. The increase of the length of the fibers by swelling in water was about 26%, exactly the same amount as the increase of the width. By stretching the xanthate from which the fibers were prepared he oriented the fibers. With increasing orientation the swelling became more and more anisotropic; finally, the swelling in length was reduced to about 1%, but the swelling in width increased to 40%. The amount of water taken up therefore remained practically unchanged. Normal viscose rayon fiber shows about 4 to 7%, and highly oriented viscose rayon shows 0.7 to 2%, axial swelling.

If the amorphous regions are regarded as the adsorbing portion of the

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[60] P. H. Hermans, *Kolloid-Z.*, **86**, 107 (1939).

cellulose material, the capacity for swelling is a measure of the relative amount of the amorphous region. Consequently, the higher sorption by mercerized and regenerated cellulose in comparison with cotton is an expression for the higher relative amount of noncrystallized material in the former. The higher values for differential contraction and differential heat of swelling of regenerated cellulose at the same moisture content are readily explained by this assumption. In the case of cotton, as outlined by Walker,[61] a part in the take-up of water may be played by the surfaces of the fibrils. As mentioned above, the latter structures have been demonstrated histologically. It is not impossible, in fact, that the microscopic discontinuities of the structure are favored by the sorption. However, fibers of regenerated cellulose take up water in a manner similar to that of the native fibers, though containing no fibrils.

(*d*) *Source of Sorption Hysteresis*

A satisfactory elucidation of the phenomenon of sorption hysteresis, for the case of rigid, inextensible gels, may be made on the basis of the theory of capillary condensation.[62] The determining factor is supposed to be the difference in curvature of the liquid surfaces in the pores during adsorption and desorption. This explanation is inapplicable to the case of gels capable of swelling, including textile fibers. For the latter, the most probable source of hysteresis is that proposed by Urquhart.[63]

The take-up of water is conceived by Urquhart as a saturation of the secondary valences of the cellulose hydroxyls. It is assumed that interaction with water is possible only to those cellulose molecules which are on the surfaces of crystallites (or, according to modern ideas, to the portions of cellulose chains in the disordered regions between the sections of regularity). The affected hydroxyl groups are freed again on drying. The cellulose molecules then try to attain positions such that there is the greatest possible mutual satisfaction of secondary valences Because of the relative immobility of the long molecules, it is not possible for them to reach the arrangement of true minimum potential energy. If the fiber is again brought into contact with water vapor, the fiber molecules try to come into as complete a contact as possible with the water molecules; that is, they tend to become independent of each other. However, in consequence of the inertia-like effect just mentioned, the positions of the cellulose molecules

[61] A. C. Walker, *Textile Research*, **7**, 229, 289 (1937).
[62] R. Zsigmondy, *Z. anorg. Chem.*, **71**, 356 (1911).
[63] A. R. Urquhart, *J. Textile Inst.*, **20**, T125 (1929).

at the same relative humidity are, after drying, less favorable to taking up water than before drying. The simplest way to express this idea is perhaps to say that on desorption the fiber contains a higher amount of disorganized material. This explains also why on desorption at the same moisture content the differential heat of swelling is higher than on adsorption, as demonstrated by Simril and Smith.[22] The fiber behaves on desorption like a material with a higher amount of amorphous region.

These ideas explain further why cotton fibers freshly removed from the seed give sorption isotherms lying well above the standard sorption loops. The primary desorption curve is particularly high. The cotton fiber grows, of course, under conditions of steady water supply from the plant, so that the cellulose chains are originally arranged favorably for large interaction with water. Analogously, mercerized cotton shows unusually high water-binding capacity before its first drying after the alkali is washed out. On the other hand, the sorptive ability of cotton is reduced by high-temperature drying.

Hamm and Patrick[64] stated that, in the complete absence of air and other indifferent gases, hysteresis vanishes. This result could not be confirmed by Walker, Campbell, and Maass.[65]

(*e*) *Dimensions of the Channels in Swollen Fibers*

The size of the submicroscopic channels in both native and regenerated celluloses is of great importance because all the reagents with which the celluloses are treated can penetrate the fiber or film only through these openings. For ramie and for viscose rayon, rough values of pore size may be estimated from x-ray measurements of crystallite size and, thus, from the distances between crystallites, or the dimensions of the amorphous regions. If it is assumed that the crystallites are spaced 60 Å. in ramie; then the take-up of even 5% of water would be sufficient to provide a monomolecular layer of water over the undisturbed sections. A take-up of 20% would require pores of 30 Å. average width. In viscose rayon, the estimated distance of centers of disturbed regions is 40 Å., and pore diameters of 30 Å. would require a 45% water content. It is, however, not known whether the irregular regions are all swelled to equivalent extents. Perhaps some of them are practically unaffected.

In the case of thin sheets, several methods, fortunately, are available for the study of the system of water-filled lacunae which results from the

[64] H. A. Hamm and W. A. Patrick, *Textile Research*, **6**, 401 (1936).

[65] F. Walker, W. B. Campbell, and O. Maass, *Can. J. Research*, **B15**, 340 (1937).

swelling. Foils of regenerated cellulose made by the viscose process are very similar in structure to viscose rayon. The dyeing behavior of the two, for instance, is practically identical. In turn, it is close to that of mercerized cotton, and not very different from that of ordinary cotton. It follows that cellulose foil is able to render valuable service as a model in the investigation of cellulose fibers.

An effective average cross section for pores traversing the sheet may be found by determining the smallest pressure at which air can be blown through the wet membrane.[66] Passage of air is resisted by the surface tension of the fluid. For convenience in computation, the pores are assumed to be right circular cylinders. Then $r = 2\sigma/P$, where r is the effective average pore radius, σ is the surface tension, and P is the required pressure. To blow nitrogen through a water-swollen membrane of du Pont No. 600 cellophane, 50 to 70 atm. was required.[67] The corresponding pore diameters are 40 to 60 Å. According to this result, the membrane should be permeable to molecular solutions, but not to the usual colloids. This expectation was confirmed by experiment. Pressure filtration of a soap solution containing colloidally and molecularly dispersed material gave a filtrate containing only the latter.

On the other hand, McBain and Stuewer[68] observed that cellophane of more recent manufacture partially retains even molecularly dispersed material. Impoverishment of the filtrate was found to the extent of 2% for dilute glycerin, 7% for dextrose solution (six carbon atoms for each molecule), 15% for sucrose (twelve carbons), and 18% for raffinose (eighteen carbons). Apparently cellophane contains a corresponding fraction of pores capable of trapping the molecules mentioned.

Another method for estimating pore size employs a comparison of the water content of the membrane with the permeability for water.[66, 69] Here, also, it is necessary to assume a shape for the pores which traverse the membrane. Then the Hagen-Poiseuille law may be used to find a relation between the hydrostatic pressure, the velocity of flow, and the diameter of the effective average pore. For a capillary crack with parallel sides,

$$\beta = \sqrt{4.5 \cdot q \cdot t \cdot \eta / w} \qquad (7)$$

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[66] H. Bechhold, *Z. physik. Chem.*, **60**, 257 (1907); **64**, 328 (1908).

[67] J. W. McBain and S. S. Kistler, *J. Gen. Physiol.*, **12**, 187 (1928); *Trans. Faraday Soc.*, **26**, 157 (1930).

[68] J. W. McBain and R. F. Stuewer, *J. Phys. Chem.*, **40**, 1157 (1936).

[69] N Bjerrum and E. Manegold, *Kolloid-Z.*, **43**, 5 (1927).

where β is the half-width, q the velocity of discharge, η the viscosity, t the thickness of the wet membrane, and w the water content in cc. for each cc. of membrane. For circular cross sections,

$$r = \sqrt{24 \cdot q \cdot t \cdot \eta / w} \tag{8}$$

where r is the radius of the capillary, and the other quantities have the same meaning as before.

Manegold and Viets[70] used this method to study a cellophane sheet (Kalle). When dry, it was 30 μ thick. In water, its thickness doubled, but the surface increased only 40% (swelling anisotropy). The foil then contained 0.855 g. water for each cc. Under the pressure of a water column 1 cm. high, the transmission of water was 5.5×10^{-9} cc. for each cm.^{2} area for each second. Under the assumption of columnar structure, with a random distribution of parallel-sided pores, the latter would require an effective half-width of about 6 Å. to fit the data. Circular pores would be 26 Å. in diameter. Applying this method to a Courtauld's Viscacelle sheet 25 μ thick, Morton[71] found similar values, 6.6 to 30 Å. It should be recognized that the distribution of the channels is not uniform. The anisotropy of swelling shows that more of the pores lie parallel to the surfaces of the foil than at right angles to it. For transfer of water, the only effective channels are those connecting the opposite sides of the sheet. Nevertheless, in the mathematical analysis, account was taken of the total water content of the sheet and not of the actual water content effective in the diffusion. When the latter is substituted for the former, the calculated average diameter of the effective pores becomes about twice as large, or 50 to 60 Å., in good agreement with the values indicated by other methods.

Determination of the velocity with which a solute diffuses through a membrane also furnishes a useful method for characterization. The dialysis coefficient δ is defined as the number of moles of solute dialyzing through 1 cm.^{2} of membrane in 24 hours, for a concentration difference of 1 mole for each liter at the membrane. It is simply related to the free diffusion coefficient D by the relation

$$D = K \cdot \frac{d\delta}{W} \tag{9}$$

where d is the thickness of the membrane, W is the water content in mg.

[70] E. Manegold and K. Viets, *Kolloid-Z.*, **56**, 7 (1931).
[71] T. H. Morton, *Trans. Faraday Soc.*, **31**, 262 (1935).

for each cc., and K is a numerical constant dependent upon the structure assumed for the pore system.

Manegold and Viets[70] determined the dialysis coefficients of urea through the same cellophane foil for which the water transmission was discussed above. The coefficient of free diffusion, computed for pores having parallel sides and for pores of circular cross section, was found to be, respectively, 0.0998 and 0.199 cm.^{2} for each day. The actual value is 1.02 cm.^{2} for each day, five or ten times the computed. The diffusion of urea through the membrane is thus hindered much more than one would expect, in view of the large water content of the membrane. This result also shows that the angular distribution of channels is nonuniform, and that only a small fraction of the total water content is effective in dialysis.

It must be noted that the permeability of cellophane is closely related to its swelling. Under a given pressure, water is forced through cellophane much more quickly than is a nonaqueous solvent such as ethanol or xylene, which generally produces only slight swelling. If the foil is first swelled in water, ethanol will, because of its lower viscosity, flow through even faster than water. On the other hand, it is found that pentanol can be pressed through a water-swollen foil only at a very slow rate. However, by replacing the swelling water by ethanol, it is possible to filter pentanol or even aniline. In order to maintain the permeability, the swelling liquid should be replaced only by another in which it is completely miscible. If the membrane is incompletely swelled by water in the first step, its permeability for organic liquids in the later processes is lowered. It is thus possible to produce cellophane membranes of controlled porosity. The pores which allow permeation of the membrane are therefore not preexistent, but are created or opened by the swelling process.

Dry cellophane, indeed, is practically impermeable even to gaseous nitrogen. For a water-swollen membrane, as noted above, a pressure of 50 atm. will cause the passage of nitrogen. At a pressure of 78 atm., the flow velocity of nitrogen relative to that of water indicates that about half of the pores are open.[67] The first passage at 50 atm. corresponds to a theoretical pore diameter of 60 Å., while that at 78 atm. corresponds to about 40 Å.; so that the observations suggest considerable uniformity of pore sizes in swollen cellophane.

Analogous behavior of viscose threads was demonstrated by Morton.[71] In water, the fibers swell to a water content of 0.85 g. for each g. of dry weight. In ethanol, the take-up of liquid is only 11%. However, if the water-swollen fiber is soaked in ethanol, 0.45 g. of the latter enters each gram of fiber.

Trillat and Matricon[72] have shown that anhydrous cellophane is impermeable to air and that, with increasing moisture content, the permeability for air becomes greater. Hydrogen also, according to the observations of deBoer and Fast,[73] is completely blocked by viscose-process foils. These observers found that cellulose nitrate and acetate films, on the other hand, will pass hydrogen but not air. Their observations confirm the assumption that systems of cavities within fibers are produced by swelling, but do not exist in the dry material.

Kistler[74] prepared cellophane with air-filled cavities. He treated water-swollen foils with a solvent capable of mixing with and displacing the water, then with liquid propane. The latter was removed above its critical temperature, with practically no resultant collapse of the expanded cellulose structure. This aerogel, however, on being wetted and then dried, underwent collapse to its original dimensions.

Campbell and Russell[75] used the method of successive replacement of swelling fluids in an attempt to settle the question of the true density of cellulose. It was mentioned previously that standard cellulose shows a specific volume of 0.64 in helium, acetone, and benzene, but only 0.62 in water. Campbell found a specific volume of 0.62 also for cellulose which had been swelled in water, then soaked successively in acetone and benzene. This would indicate definitely that the lower density results from incomplete entry of the pycnometric fluid into the cavities of the fiber and that the density found in water is the true one. The contraction determined for water take-up then would become illusory.

Stamm and Hansen[55] rejected this conclusion, having reasons to assume that water is replaced only incompletely by substitution of another swelling liquid. A further convincing argument, they have found, for the reality of the contraction is a constant ratio of internal pressure to heats of mixing of liquids.

Repeated attempts have been made to determine the inner surface of cellulose by measurement of the amount of sorbed gases, liquids, or dissolved substances. These approximations generally use the assumption of a complete monomolecular coating, for which there is seldom evidence. As a matter of fact, the results so obtained are inconsistent.

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[72] J. J. Trillat and M. Matricon, *J. chim. phys.*, **32**, 101 (1935).

[73] J. H. deBoer and J. D. Fast, *Rec. trav. chim.*, **57**, 317 (1938).

[74] S. S. Kistler, *J. Phys. Chem.*, **36**, 52 (1932).

[75] W. B. Campbell and J. K. Russell, *Quart. Rev. Forest Prod. Lab. Can.*, **21**, 24 (1935).

4. Effect of Moisture on the Mechanical and Electrical Properties of Cellulose Fibers

The ratio of the breaking strength of a fiber in the wet (water-swollen) state to that in dry state (which generally means a moisture content corresponding to 60 or 70% RH) is denoted as relative wet strength. Char-

TABLE 11

RELATIVE WET STRENGTH OF CELLULOSE FIBERS (OBERMILLER AND GOERTZ[76])

Fiber	Wet strength, %
Cotton	110–120
Cuprammonium rayon	50–60
Viscose rayon	45–55
Acetate rayon	65–70

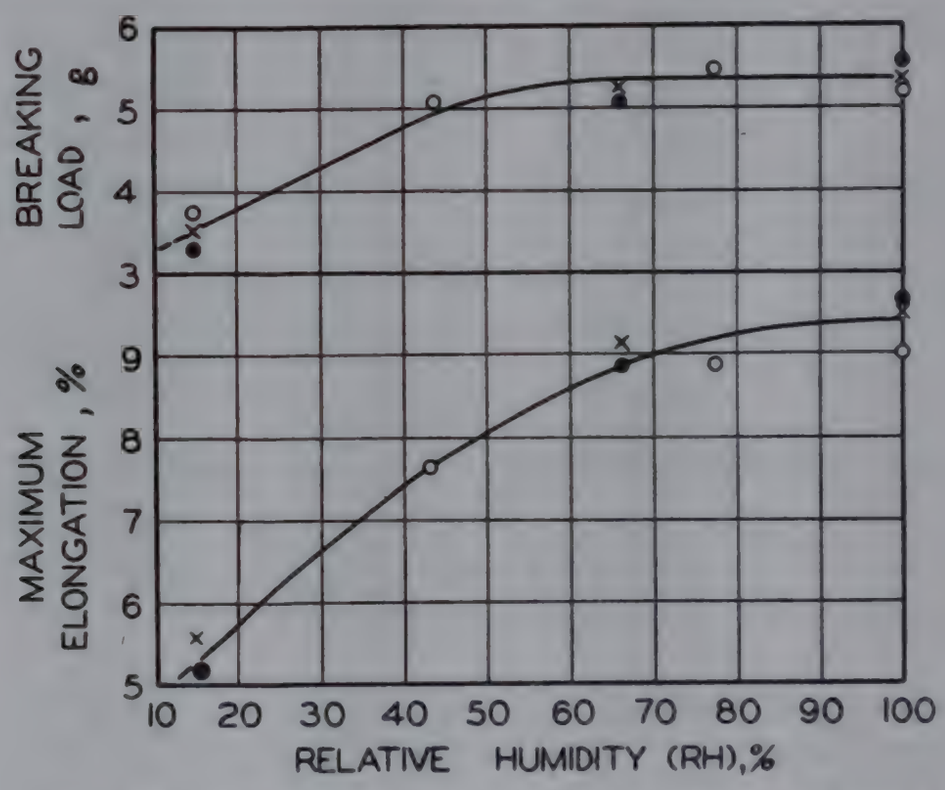

FIG. 87.—TENSILE STRENGTH AND ELONGATION OF SINGLE COTTON FIBERS AS A FUNCTION OF RELATIVE HUMIDITY (BROWN, MANN, AND PEIRCE[77]).

acteristic values of the relative wet strength of cellulose fibers are to be found in Table 11.[76] From these data three facts are evident: the tensile strength of native cellulose fibers is higher in the wet state than in the dry

[76] J. Obermiller and M. Goertz, *Melliand Textilber.*, **7**, 71 (1926).

[77] K. C. Brown, J. C. Mann, and F. T. Peirce, *J. Textile Inst.*, **21**, T187 (1930).

tate; the tensile strength of cellulose acetate is diminished to a moderate extent by swelling; the tensile strength of regenerated cellulose fibers is considerably diminished by swelling.

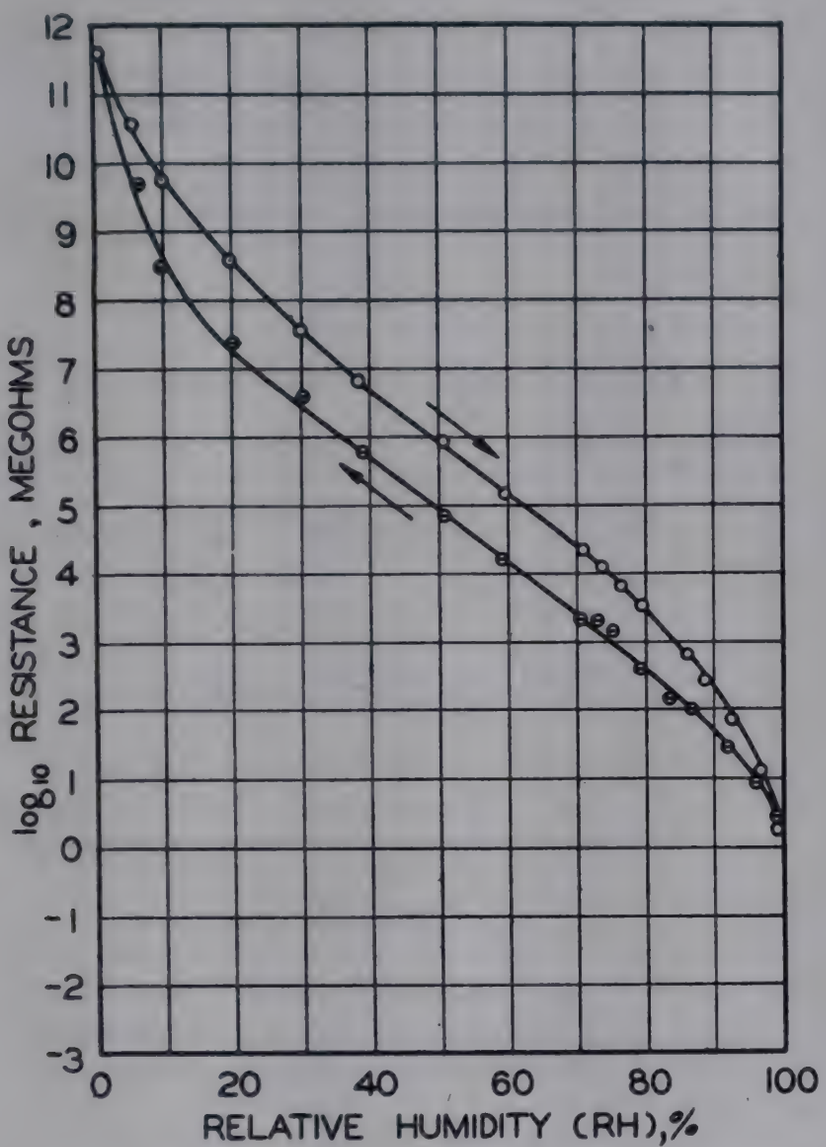

FIG. 88.—INSULATION RESISTANCE OF COTTON THREADS AS A FUNCTION OF RELATIVE HUMIDITY (MURPHY AND WALKER[78]).

Brown, Mann, and Peirce[77] carried out 600 single breaking strength tests on cotton fibers, covering the whole range of relative humidity. Their results are plotted in Figure 87.

The decrease of the tensile strength of regenerated cellulose by swelling is easily explained on the assumption that the cohesion of fiber material is diminished as a consequence of separation of fiber molecules by water

[78] E. J. Murphy and A. C. Walker, *J. Phys. Chem.*, **32**, 1761 (1928)

molecules. More difficult to explain is the increase of the strength o native fibers by swelling. Probably the lower modulus of elasticity (higher elongation) in the wet state, as demonstrated in Figure 87, per mits a more uniform distribution of the strain than is possible in the rela tively rigid dry fiber. Further treatment of the mechanical behavior o fibers is given in Chapter IX, G, 2, on "Elasticity and Strength."

The electrical resistance of cotton fibers is extremely sensitive to change of the moisture content. Figure 88 is a graph by Murphy and Walker[7] which demonstrates that the electrical resistance of cotton fibers in the

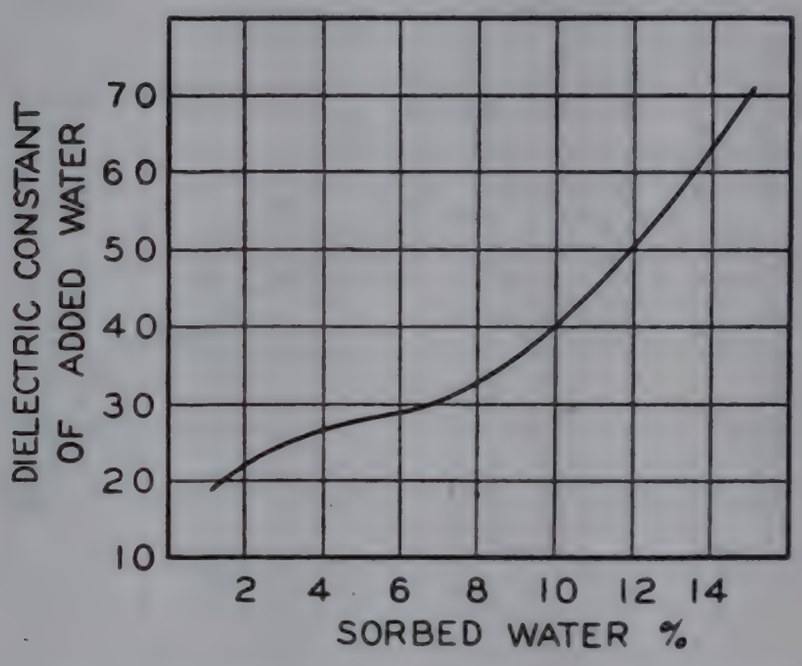

FIG. 89.—DIELECTRIC CONSTANT OF WATER SORBED BY COTTON AS A FUNCTION OF MOISTURE CONTENT (DIFFERENTIAL VALUES) (ARGUE AND MAASS[80]).

direction of their axis diminishes between 6 and 98.6% RH in a ratio of $1 : 10^{10}$. Hysteresis is pronounced in this case also. However, if the resistance is plotted against the moisture content and not against the relative humidity, the adsorption and desorption curves are very close. In the region of intermediate humidity the logarithm of the electrical resistance is a linear function of the logarithm of relative humidity.

Obviously, the cellulose itself is a good insulator and the conductivity of the fibers depends on the moisture content. O'Sullivan[79] suggests that the frictional resistance of the electrolytic transportation of ions in the

[79] J. B. O'Sullivan, *Trans. Faraday Soc.*, 29, 192 (1933).

[80] G. H. Argue and O. Maass, *Can. J. Research*, **13B**, 156 (1935).

water-filled channels of the fibers determines the electrical resistance. The change of the diameter of the pores with increasing sorption is responsible for the change of the frictional, and consequently of the electrical, resistance.

Argue and Maass[80] measured the dielectric constant of cotton varying in moisture content. They calculated the dielectric constant of the adsorbed water as a function of the moisture content (Fig. 89). The dielectric constant of the water first sorbed was found to be very much less than that of free water; approximately that of ice at low temperatures. These results indicate that the first water molecules which are adsorbed are anchored into fixed positions and that the orientation of subsequently adsorbed water molecules gradually diminishes until they are able to rotate as in free water.

Because the change in electrical conductivity of fibers with the changes of the moisture content is so great, the electrical properties can be used as a means of determining the moisture content of the cellulose.[81]

To summarize, the sorption of liquids and vapors, especially water, by cellulose is of great practical importance because the presence of water increases the penetration of reagents into the cellulose, increases the electrical conductivity, and changes the breaking strength and other mechanical characteristics. The amount of adsorption varies with the type of cellulose and the treatment it has undergone, regenerated and mercerized cottons adsorbing the most, and, consequently, the effects of moisture vary also with the cellulose. A knowledge of the sorption process, therefore, enables a definite amount of control over these important physical and chemical properties.

[81] A. J. Stamm, *Ind. Eng. Chem.*, **19**, 1021 (1927).

Chapter IV

CARBOHYDRATES NORMALLY ASSOCIATED WITH CELLULOSE IN NATURE

CARBOHYDRATES NORMALLY ASSOCIATED WITH CELLULOSE IN NATURE[1]

A. G. NORMAN

A. SUGARS FOUND IN HEMICELLULOSES AND RELATED POLYSACCHARIDES

The primary photosynthetic product of green plants is probably a hexose sugar, either glucose or fructose, and the former appears as the building unit of the two polysaccharides that have major roles in the plant, namely, cellulose as a structural constituent, and starch as a reserve. However, other polysaccharides associated with cellulose in the cell wall or present like starch in the cell may contain and indeed are often exclusively composed of sugar units other than glucose. Conversion of one hexose into another is presumably easily accomplished in the plant, though of the possible aldo- and keto-hexoses, 24 in all, only five are known to occur naturally in plants, and of these, three have been found only in polysaccharides. The five are *d*-glucose, *d*-fructose, *d*-mannose, *d*-galactose, and *l*-galactose, the last being very rare. The transformation from the normal form of glucose to mannose or galactose involves a transposition of OH and H groups on carbon atom 2 or 4. This may not necessarily occur only when a sugar is in a monosaccharide condition, and indeed the fact that neither *d*-mannose nor *d*-galactose have been identified as free sugars in plant tissues suggests that the transformation does occur when a sugar is linked in a polysaccharide condition, or at the time of polysaccharide synthesis.

Pentose and uronic units also are common in polysaccharides of plant origin, and since the assumption seems always to be made, on grounds similar to those above, that pentose sugars are not direct products of photosynthesis, their formation from hexoses is inferred. Of the possible aldohexuronic acids and pentoses only three of the former and two of the latter seem to occur in plant polysaccharides. These are *d*-glucuronic

[1] For a more comprehensive treatment of the relationship between hemicelluloses and the somewhat similar gums, mucilages, pectins, etc., see A. G. Norman, *The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.* Clarendon Press, Oxford, 1937.

acid, *d*-galacturonic acid, *d*-mannuronic acid (the last only in certain marine algae), *d*-xylose, and *l*-arabinose. It will be seen (Fig. 1) that configurationally these are directly related to the three aldohexoses mentioned above. Two series seem to be complete, namely, the glucose-glucuronic

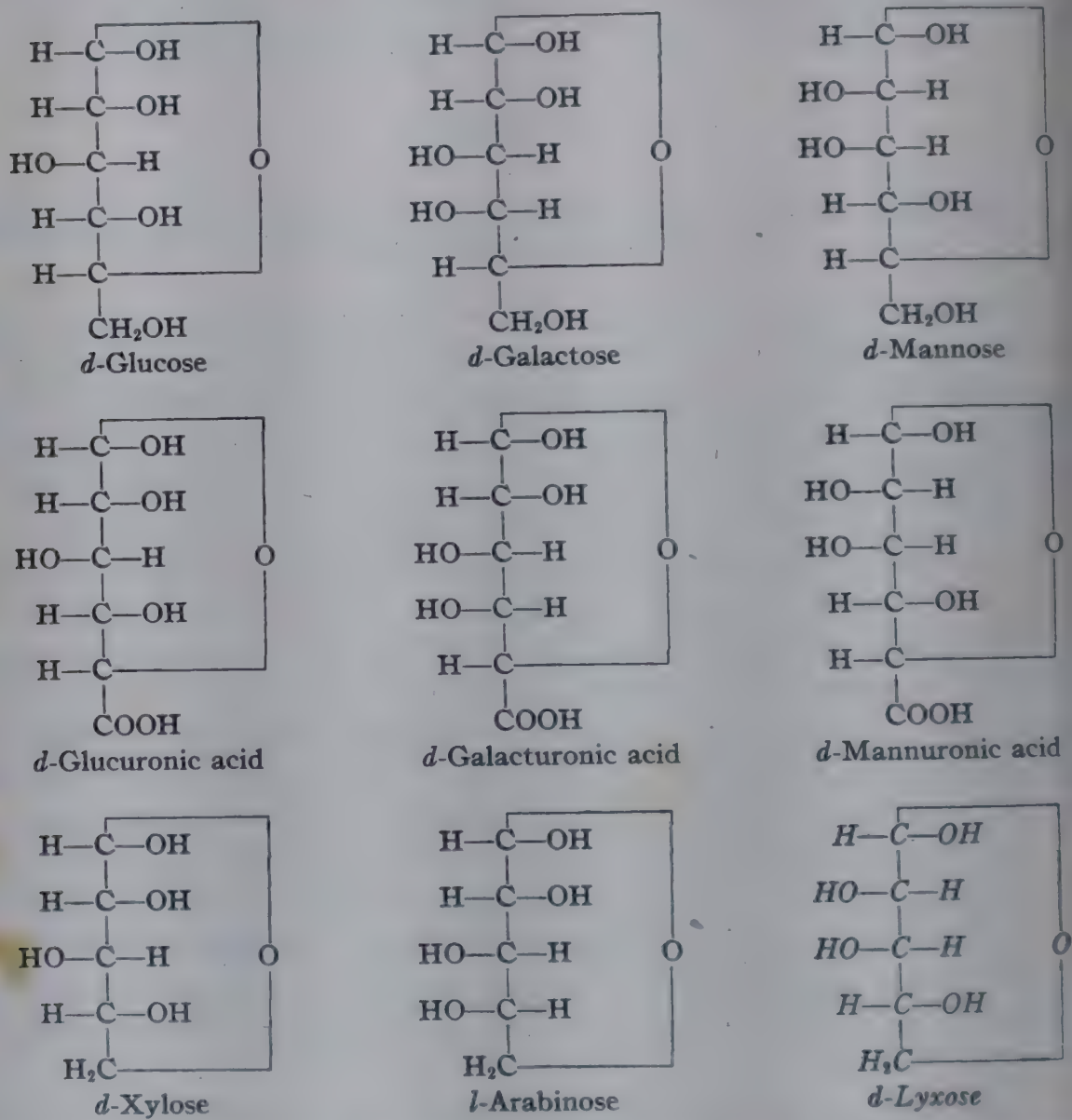

FIG. 1.—CONFIGURATIONAL RELATIONSHIPS OF SUGARS FOUND AS CONSTITUENT UNITS IN PLANT POLYSACCHARIDES (PYRANOSE FORM).

xylose series and the galactose-galacturonic-arabinose series. It is probably significant that in some polysaccharides these sterically related sugars are present together as constituent units. For example, hemicelluloses have been isolated containing glucose, glucuronic, and xylose groups, the last predominating. Pectin appears to be a polygalacturonide, but

usually associated with araban and galactan. Water-soluble arabogalactans are present in larch wood. Such observations make plausible the theory of a hexosan → hexuronide → pentosan transformation, though the evidence is little more than presumptive. The mannose series is incomplete in that the corresponding pentose, *d*-lyxose, is unknown, and the uronic acid of the series, *d*-mannuronic acid, has been found only in the polysaccharide alginic acid isolated from certain marine algae. In plants containing mannan, such as conifers, no mannuronic acid has ever been identified.

Too little is known of the steps involved in synthesis of polysaccharides to allow a decision to be reached as to whether an existing hexosan can be completely converted *in situ* into a polyuronide or pentosan by oxidation and subsequent decarboxylation. Sterically this might be possible, and indeed xylan has been said to be formed from cellulose by such a transformation. By incomplete oxidation and decarboxylation it is conceivable that polysaccharides containing hexose, hexuronic, and pentose groups might be obtained that would resemble in analysis certain hemicellulose preparations. However, in the few structurally nonhomogeneous or mixed polysaccharides about which some constitutional information has been obtained, some constancy of structure is apparent. Particular groups seem to occupy particular positions, and chains are invariably terminated in a uniform manner. This would suggest that such polysaccharides are not the products of *in situ* transformations but are synthesized enzymatically from comparatively small units.

B. HEMICELLULOSES

1. Definition and Occurrence

The cellulosic fabric in the primary and secondary cell walls of plants forms a continuous system, which is, however, porous or sponge-like in that communicating interstices are present. In these elongated spaces are deposited the amorphous cell-wall constituents, mainly lignin and polysaccharides that are described as hemicelluloses. These noncellulosic unoriented components similarly form a more or less continuous interpenetrating system, and no doubt have a stiffening effect on the wall as a whole. The three major constituents of the mature cell wall, namely, cellulose, hemicelluloses, and lignin, are therefore in the closest physical association, and inasmuch as some of their chemical properties overlap, sharp separation is a matter of considerable difficulty. The distinction between cellulose

and hemicelluloses was made first by Schulze,[2] on the basis of the solubility of the latter in dilute acids. It was his belief, however, that the hemicelluloses were closely related to cellulose both chemically and functionally, hence the similarity in nomenclature. His studies were mostly carried out with seeds in which he believed the hemicelluloses act also as reserve carbohydrates.

Definitions based largely on properties are rarely wholly satisfactory, yet even now it is not possible to provide an alternative omitting properties entirely. In its present usage the term hemicelluloses includes those cell-wall polysaccharides which are removable by cold or hot alkali, and which may be hydrolyzed by boiling with dilute acids to give constituent monosaccharide units. More than one sugar may be found on hydrolysis, and hexuronic groups may also be present. This definition of the hemicelluloses causes to be included together polysaccharides of at least two types with different roles and from different locations in the cell wall. There is no doubt that an attempt should be made to distinguish between these two types of polysaccharides in all chemical studies on plant materials, even though it may not be possible to separate them in an alkaline extract. Under the general title of hemicelluloses there are included, therefore, those amorphous polysaccharides that formed a part of the system interpenetrating and incrusting the cellulosic fabric, and also those short-chain polysaccharides that originally formed a part of the cellulosic fabric itself. The latter exist only associated with cellulose until extracted, and *in situ* are oriented in the micellar structure.

Representatives of these two groups exhibit certain chemical differences. Uronic groups seem to be characteristically present in the incrusting polysaccharides and for this reason they are sometimes referred to as "polyuronide hemicelluloses." Only glucuronic and galacturonic acids have been authentically reported. (See refs. on pp. 441 *ff*.) The accompanying sugar units commonly found may be either hexoses or pentoses or both. Evidence has been presented in support of the view that the polyuronide hemicelluloses may normally be linked to lignin, though it is by no means certain that this is invariably or exclusively the case. (See pp. 433-35 where the evidence is fully discussed.) The study of the polyuronide hemicelluloses has been much hampered by the fact that preparations have also contained polysaccharides concurrently extracted from the cellulose. These have been termed "cellulosans" and do not characteristically contain hexuronic units, although a few carboxyl groups of this type may be present.

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[2] E. Schulze, *Ber.*, **24**, 2277 (1891).

On hydrolysis, one, or at most two, sugars are obtained. The cellulosans, therefore, seem to be relatively simple hexosans or pentosans. The cellulosan fraction of angiosperm plants seems usually to be predominantly a xylan, though there may be present also some glucosan that probably represents very short cellulose chains. The cellulose of gymnosperms (softwoods) has usually a considerably lower xylan content and, in addition to the glucosan just referred to, it also contains a mannan. The study of the cellulosans is far less difficult than that of the polyuronide hemicelluloses because they may be obtained directly in a relatively pure condition by the alkaline extraction of cellulose prepared by the chlorination procedure that is the basis of the Cross and Bevan method for the determination of cellu-

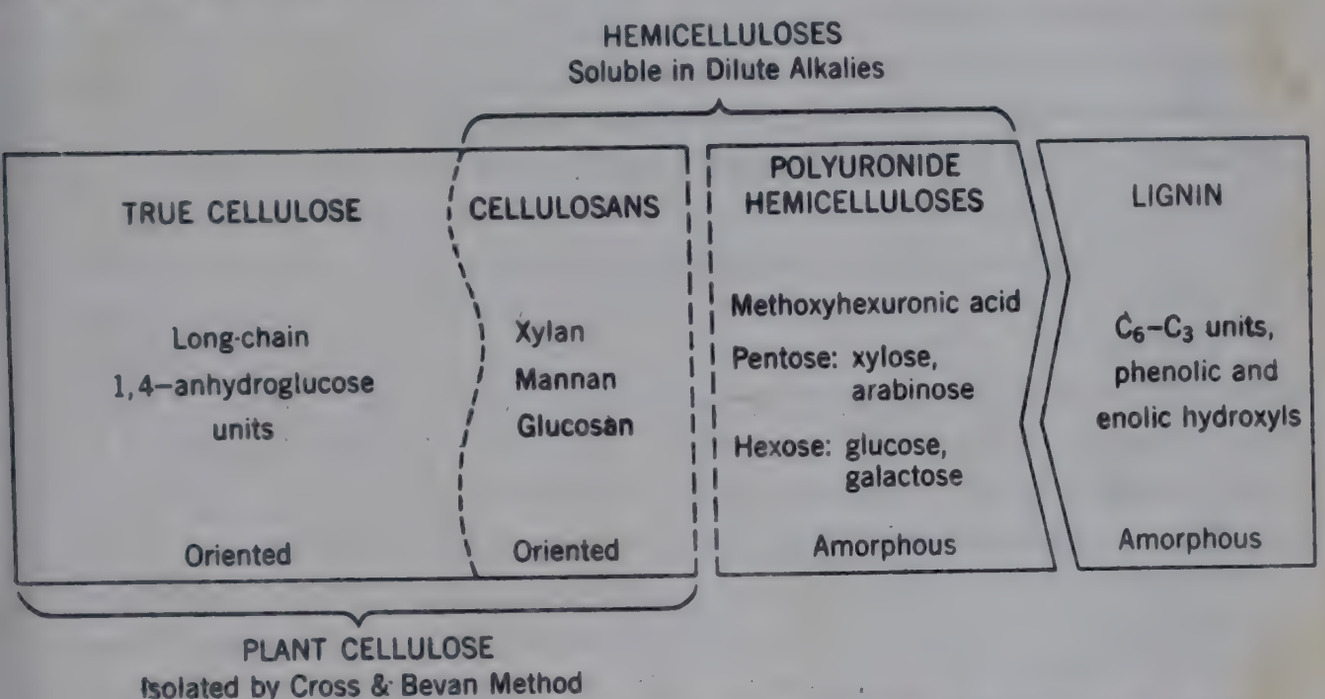

FIG. 2.—DIAGRAM ILLUSTRATING RELATIONSHIPS BETWEEN MAJOR CELL-WALL CONSTITUENTS.

lose. They form in the main that indefinite fraction of pulps known industrially as beta- and gamma-cellulose.

The relationships between the major cell-wall constituents as outlined above are indicated, highly diagrammatically, in Figure 2. The separation of the hemicelluloses into two groups, (1) the cellulosans, and (2) the polyuronide hemicelluloses, rests primarily on the Cross and Bevan cellulose method (see Chapter II, F) which involves the use of neutral reagents only. It cannot be said, however, that the line of division between these two groups is extremely sharp since the pretreatment of the material affects the subsequent partition. Kiln-drying of wood, for example, has been shown to affect the separation by reducing the amount of cellulosan isolated

with the cellulose.[3] Pretreatments with dilute alkali[4] or alcoholic sodium hydroxide,[5] on the other hand, cause some of the polyuronide hemicelluloses to be retained with the cellulosans, as judged by an increased furfuraldehyde yield from the cellulose product. Similarly, extraction with ethanolamine, followed by chlorination and treatment with sodium sulfite to remove lignin and polyuronide hemicelluloses,[6] leaves a residue that has a higher pentosan content than the cellulose fraction obtained by the Cross and Bevan procedure.[7]

For various reasons, it is not possible to give accurate figures for the total amount of hemicelluloses present in plant materials. There is no simple extraction method which will remove quantitatively all hemicelluloses without affecting other constituents, nor is it easy to see how any simple method can be devised to determine polysaccharides with more than one constituent sugar. Several procedures involving dilute acid hydrolysis and titration of reducing groups have been proposed but none are satisfactory. The hydrolytic treatment fails to separate the cellulosans from the incrusting polyuronide hemicelluloses, but for some purposes this may be an unimportant objection. More serious is the fact that the hydrolysis of the polyuronide hemicelluloses does not proceed smoothly to completion. Resistant aldobionic acids may be present which will survive boiling for many hours. Liberated uronic acids, however, are decarboxylated under such conditions, and pentose sugars are slowly destroyed. Complete recoveries of reducing sugars from hemicelluloses are, therefore, not obtained.

Both Preece[8] and Buston[9, 10] have attempted hemicellulose determination by isolating the carbohydrates quantitatively on a small scale. The procedure is tedious and applicable only to special problems. Corrections have to be applied for lignin, protein, and ash, some of each of which may be present in the preparations. These, of course, include both cellulosans and polyuronide hemicelluloses, and the complete picture is not obtained unless the residue is examined also.

The most satisfactory approach to the problem of hemicellulose deter-

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[3] W. G. Campbell and J. Booth, *Biochem. J.*, **24**, 641 (1930); **25**, 756 (1931).

[4] A. W. Mackney, *J. Council Sci. Ind. Research*, **13**, 115 (1940).

[5] I. A. Preece, *Biochem. J.*, **35**, 659 (1941).

[6] L. E. Wise, F. C. Peterson, and W. M. Harlow, *Ind. Eng. Chem., Anal. Ed.*, **11**, 18 (1939).

[7] J. D. Reid, G. H. Nelson, and S. I. Aronovsky, *Ind. Eng. Chem., Anal. Ed.*, **12**, 255 (1940).

[8] I. A. Preece, *Biochem. J.*, **25**, 1304 (1931).

[9] H. W. Buston, *Biochem. J.*, **28**, 1028 (1934).

[10] H. W. Buston, *Biochem. J*, **29**, 196 (1935).

mination perhaps lies in separate analyses for particular groups known to be present, and this in fact is the method commonly employed in plant analysis. Under certain circumstances, the figures so obtained may not be far short of the actual totals. The total pentose content of the material, and that of the Cross and Bevan cellulose isolated therefrom, are separately ascertained, thus giving by difference the pentose groups in the polyuronide hemicellulose fraction. Uronic determinations may also be carried out, preferably after extraction with 0.5% ammonium oxalate to remove pectic substances. These three determinations are sufficient to characterize many mature materials, inasmuch as the polyuronide hemicelluloses are frequently xylan-glucuronides with xylose units predominating and the cellulosan similarly is predominantly a xylan. In softwoods, mannan may be present with xylan in the cellulosan fraction and this can be determined with a fair degree of accuracy.[11] Hexose units such as glucose or galactose in the polyuronide hemicelluloses are at present indeterminable. Glucose is rarely an important constituent but galactose may be a major constituent in hemicelluloses of the galactan-araban-galacturonide type, which are more frequently found in green unlignified tissues.[10]

In general, it seems that the total hemicellulose content of plant materials falls within the range of 15 to 30% and, of that present, as much as one-half may be cellulosan. The relationship between polyuronide hemicelluloses and cellulosans is by no means a constant one during development and maturation of a tissue, although there is not usually any pronounced or greatly disproportionate change.

2. Relationship Between Hemicelluloses and Other Cell-Wall Constituents

(a) *Polyuronide Hemicelluloses*

The behavior of the polyuronide hemicelluloses in respect to extracting agents cannot be explained without assuming linkage to some other cell-wall constituent, probably lignin (see Chapter II, E). Some variation in solubility would be expected if polysaccharides of different chain length or different degrees of molecular aggregation were present, but this is insufficient to account for the fact that the polyuronide hemicelluloses cannot be extensively or completely removed from lignified tissues without the applica-

[11] A. Nowotnowna. *Biochem. J.*, **30**, 2177 (1936).

tion of a treatment that might dissociate a linkage with lignin. Similarly, lignin cannot be removed without simultaneous liberation or decomposition of these polysaccharides. The lignin-polyuronide hemicellulose complex cannot be separated unchanged for direct study, though the isolation of a small amount of a lignin-carbohydrate compound has been reported.[12] A glycosidic linkage is probably involved,[13] but it is most unlikely that the combining power of the one component for the other component is satisfied at all times. Moreover, the homogeneity of lignin is by no means assured. The form of association between lignin and hemicelluloses is therefore likely to be highly complex. This is fully in line with observations on the extraction of the latter with alkali which brings about solution of the hemicelluloses to an extent depending on the concentration, temperature, and time. The extent of extraction by cold alkali is much increased if preceded by chlorination and this fact has been utilized in preparational work.[14]

Further evidence for the existence of a lignin-hemicellulose linkage has been obtained by following the removal of hemicelluloses during the isolation of Cross and Bevan cellulose.[15] They pass into solution in sodium sulfite along with the lignin only if the sulfite treatment is preceded by chlorination. To a considerable extent they are even soluble in water after chlorination, which presumably brings about rupture of the linkage with lignin. Similarly, from tissues that have been completely delignified by one of the methods for isolation of the "holocellulose" fraction (see Chapter III, B), the ease of extraction of polyuronide hemicelluloses is greatly increased. However, even then they are not of uniform and equal solubility. Some may be extracted readily with water, but dilute alkali is still necessary to effect solution of the main fraction.[16]

Various lignin reactions may be cited which also point to some form of combination with hydrolyzable polysaccharides. An enolic hydroxyl group may be involved in the linkage. Lignin in the cell wall cannot be readily methylated, whereas methoxyl groups can be easily introduced into isolated lignin or after simple acid hydrolysis of the plant material.[17] Chlorine uptake by the lignin *in situ* is also different before and after hydrolysis. The properties of lignin may change when the hydrolyzable carbohydrates are removed. Removal of lignin in the pulp-

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[12] F. E. Brauns and D. S. Brown, *Ind. Eng. Chem.*, **30**, 779 (1938).
[13] K. Freudenberg, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 34 (1938).
[14] L. Sands and P. Nutter, *J. Biol. Chem.*, **110**, 17 (1935).
[15] A. G. Norman and J. G. Shrikhande, *Biochem. J.*, **29**, 2259 (1935).
[16] R. L. Mitchell and G. J. Ritter, *J. Am. Chem. Soc.*, **62**, 1958 (1940).
[17] E. E. Harris, E. C. Sherrard, and R. L. Mitchell, *J. Am. Chem. Soc.*, **56**, 889 (1934).

ıg of hydrolyzed wood either by the sulfite process[18] or by the soda process s less complete than if normal wood is so treated.[19]

(*b*) *Cellulosans*

The form of association of the cellulosans with the cellulose is of an entirely different character and has not, in fact, been exhaustively studied. That there is no real line of separation between cellulosans and true cellulose is almost certain. The distinction is made primarily on solubility or insolubility in dilute alkali, and susceptibility or resistance to hydrolysis by dilute acid. The separation that is made is purely arbitrary and varies with the concentration, temperature, and length of treatment with the reagent. For example, the conventional procedure for obtaining alpha-cellulose does not invariably yield a product that consists only of true cellulose molecules. The cellulosans associated with the true cellulose in the cellulosic fabric are believed to be relatively short-chain compounds, the xylose, mannose, or glucose units of which have a pyranose structure, and which therefore occupy longitudinally the same space as the glucose units in the cellulose chains. These short-chain polysaccharides would therefore pack readily into the oriented cellulosic structure, the longitudinal strength of which is due to the presence of immensely long cellulose chains, between which some cross-bridging or looping may also occur. The short-chain cellulosans would be retained by such lateral forces as are operative between adjacent cellulose chains. The xylan chain would lack the projecting carbinol unit of carbon atom 6, but this does not appear to affect retention appreciably, since from softwood cellulose the xylan is not removable by alkali any more readily than the mannan.[11] Examination of the x-ray diagrams obtained from fibers before and after removal of cellulosan has shown a slight improvement in orientation, but no marked change.[20, 21] It is perhaps significant that the fibers of high tensile strength are those in which the cellulosan content is low. Cotton, ramie, flax, and hemp are almost free of cellulosan, whereas jute, sisal, Manila hemp (abaca), and coir all contain substantial amounts. The general architecture of the cellulose structure in the latter would be far less homogeneous and less uniform than that of the former because of the presence of the short-chain cellulosans.

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[18] K. Freudenberg, H. Zocher, and W. Durr, *Ber.*, **62B**, 1914 (1929).
[19] F. E. Brauns and W. S. Grimes, *Paper Trade J.*, **108**, 40 (Mar. 16, 1939).
[20] W. T. Astbury, R. D. Preston, and A. G. Norman, *Nature*, **136**, 391 (1935).
[21] R. D. Preston and A. Allsopp, *Biodynamica*, **2**, No. 53, 1 (1939).

3. Isolation and Fractionation

In investigating the hemicelluloses of plant materials, most workers have wished to study the polyuronide hemicelluloses, not the cellulosans, and have worked up their alkali extracts without having in mind the dual source of the polysaccharides actually present in them. Moreover, in many cases no attempt has been made to bring about complete or extensive extraction, though the fraction obtained has been regarded as being typical of the group as a whole. These errors would have been avoided had adequate analyses been made of the plant material before and after extraction, and this should be regarded as an essential step in any preparational work. Under certain conditions of extraction, the amount of cellulosan present in the extract may be small in comparison to the polyuronide hemicellulose, but the procedures used by some have certainly produced the opposite effect. Alkalies alone do not provide the best means of resolving the lignin-polyuronide hemicellulose linkage, and while the application of hot, relatively strong, alkaline solutions, often for many hours, may give a high yield of total polysaccharides, the contribution by the cellulosans will be at the maximum. That hemicellulose extracts are mixtures of two groups of polysaccharides of different origin would not be of consequence if they were subsequently easily separable. This, however, is not at present the case, though various fractionation procedures have been proposed, some of which will be discussed later. An entirely new approach to the problem of isolation and separation of hemicelluloses is required if much further advance is to be made. The various procedures and modifications based on direct alkaline extraction hitherto used almost exclusively leave little scope for further development and improvement. Our knowledge of the hemicelluloses is not much furthered by their continued application to additional plant materials.

The following is the general procedure that has been employed: the plant material is finely ground and treated with alcohol-benzene in a continuous extractor for many hours. After washing with alcohol and drying, the residue is treated with water below the boiling point for some hours, followed by a similar extraction with 0.5% ammonium oxalate, these treatments being applied to remove water-soluble and pectic constituents.

The dried residue is treated with alcoholic sodium hydroxide with the intention of lowering the lignin content, and so reducing the amount that passes into solution along with the hemicelluloses on subsequent extraction with alkali. The use of alcoholic sodium hydroxide was first proposed by Norris and Preece,[22] and the conditions recommended were refluxing with

[22] F. W. Norris and I. A. Preece, *Biochem. J.*, **24** 59 (1930).

50% ethyl alcohol containing 1% sodium hydroxide for two hours, followed by a further treatment for one hour with fresh solution. The time and temperature of this treatment have been varied. At boiling temperatures, however, it has been shown that a more or less serious degradative effect on the polyuronides may occur,[23] while if the extraction is carried out at room temperature[9] little removal of lignin is effected. The presence of pentose and uronide material may not be detected in the extracts, and the magnitude of the losses brought about by alcoholic sodium hydroxide can be ascertained only by analysis of the residue.[23] Preece has now presented additional evidence supporting the opinion that the grave disadvantages of such a pretreatment far outweigh its advantages in accomplishing partial delignification or partial removal of protein.[24]

The dried residue from the previous treatment is extracted several times at room temperature with 4 or 5% sodium hydroxide, and from the combined extracts the hemicelluloses are precipitated by means described below. Sodium hydroxide in the cold, however, does not bring about solution of all the alkali-soluble polysaccharides, and accordingly various workers have treated the residue further. Some have continued alkali treatment using boiling 4% sodium hydroxide, while others have increased the strength of alkali. The microscopic examination of wood sections treated with alkali in the cold indicated that a considerable part of the hemicelluloses remained undissolved, but that delignification of the residue by exposure to chlorine gas and extraction with cold 10% ammonium hydroxide then rendered the remaining hemicelluloses soluble in cold alkali.[25] This has been applied to large-scale preparational work and found to be highly effective,[14, 26] though there is some risk of loss in the ammonia extract, and the concentration of the alkali employed after delignification is probably unnecessarily high. After chlorination, direct re-extraction with cold alkali of the same concentration as initially employed may be carried out, since the lignin which concurrently passes into solution can be removed by other means later.[27] If chlorine rather than sodium hydroxide is used to dissociate the linkage with lignin, actual extraction of hemicelluloses may be accomplished with far more dilute solutions of alkali than have commonly been employed.

The hemicelluloses may be precipitated from the combined extract by

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[23] A. G. Norman, *Biochem. J.*, **29**, 945 (1935).
[24] I. A. Preece, *Biochem. J.*, **34**, 251 (1940); **35**, 659 (1941).
[25] I. W. Bailey and T. Kerr, *J. Arnold Arboretum*, **16**, 273 (1935).
[26] E. Anderson, *et al.*, *J. Biol. Chem.*, **121**, 165 (1937); **135**, 189 (1940).
[27] A. G. Norman, *Biochem. J.*, **31**, 1579 (1937).

acidification and addition of excess ethyl alcohol, but it has been customary at this point to commence fractionation. Separation into two or more fractions is accomplished by differential precipitation, but there are no criteria that may be applied to determine the purity or homogeneity of any fraction, nor in fact have identical conditions of precipitation been employed by different workers to give fractions which are described as similar. The main separation is commonly made by taking off first a fraction precipitated by the simple addition of acid to the alkaline extract. This, following the nomenclature introduced by O'Dwyer,[28] is termed hemicellulose A. Some attention has to be paid to the precise conditions of precipitation since it appears that the *p*H at which maximum yield is obtained varies somewhat with the source.[29] Excess of glacial acetic acid has sometimes been employed but, because of the buffering effect of the sodium acetate present, this may not give a low enough *p*H.

A fraction described by O'Dwyer as hemicellulose B is obtained by the addition of alcohol or acetone to the filtrate from A. Other workers have carried out a two-step separation at this stage, taking off first fraction B by the addition of half a volume of acetone or ethyl alcohol to the filtrate from A, and then fraction C by the addition of additional acetone or ethyl alcohol.[22] Each fraction is redissolved and reprecipitated several times, and further separation may be effected if desired by use of the Salkowski reaction with copper compounds.[30] Fehling's solution is added to an alkaline solution of hemicellulose, and a blue gelatinous precipitate may form. This is termed fraction A_1, B_1, or C_1, and alcohol or acetone added to the filtrate to precipitate the remainder, which is termed B_2 or C_2 (none is ordinarily obtained from the A fraction). A mixture of glycerol and cupric sulfate has been said to be more effective than Fehling's solution.[29]

The fractionation system described above has been fairly widely employed, yet sufficient variations have been introduced so that without checking details of procedure it cannot be assumed that the B_1 fraction of one worker was obtained in a manner identical to that used by another in obtaining a similarly described fraction. The entire absence of certain fractions from some materials has frequently been reported, but it must be borne in mind that these designations really indicate particular methods of precipitation only and not necessarily well-defined classes of hemicelluloses. For example, Sands and Nutter[14] obtained no B fraction in

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[28] M. H. O'Dwyer, *Biochem. J.*, **20**, 656 (1926).

[29] S. Angell and F. W. Norris, *Biochem. J.*, **30**, 2155 (1936).

[30] E. Salkowski, *Z. physiol. Chem.*, **34**, 162 (1901).

extracts from mesquite wood, Phillips[31, 32] no A or C fraction in extracts from wheat straw or alfalfa hay. Similarly, some workers on the hemicelluloses from woods similarly have obtained only two fractions, corresponding roughly to hemicelluloses A and C in the Norris and Preece system. Anderson and coworkers[33] distinguish only between the "less-soluble" and "more-soluble" portions of the hemicelluloses, but keep polysaccharides removed from the wood by direct extraction with alkali separate from those coming into solution only after chlorination. Four fractions are thus obtained; A and C in their system being "less-soluble" and therefore precipitated by the addition of half a volume of alcohol to the acidified extract before and after chlorination, respectively; B and D being "more-soluble" and therefore only precipitated by the further addition of three volumes of alcohol to the filtrates from A and C.

Inasmuch as lignin is soluble to some extent in alkali and is precipitated on acidification, hemicellulose preparations are apt to contain several per cent of lignin unless special precautions are adopted for its removal. Solution in alkali and reprecipitation several times with ethyl alcohol is fairly effective, since the lignin then remains in solution in the alkaline alcohol. An alternative method of removal is brief chlorination followed by precipitation with alcohol and repeated washing with 50–60% ethyl alcohol.[27] The delignifying procedure devised for the isolation of holocellulose[34] has been employed by Weihe and Phillips[32] for the removal of lignin from hemicellulose preparations. The precipitated hemicellulose is suspended and partially dispersed in a small volume of water. Chlorine is passed in slowly for one hour and then excess ethyl alcohol is added. The precipitate is treated twice with a solution of 3% ethanolamine in 95% ethyl alcohol at 80°C. for ten minutes. This procedure appears to be very effective in giving a product virtually free of lignin, though the length of time of exposure to chlorine is perhaps unnecessarily long.

Lignin-free holocellulose has been employed as starting material for hemicellulose extraction. Because the removal of the polyuronide hemicellulose group from such material no longer depends on the rupture of a lignin linkage, these polysaccharides are more easily soluble. The delignification process should not affect the association between cellulosans and cellulose so that no change would be expected in the properties of that group. Holocellulose preparations from hardwoods seem to retain virtually all the

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[31] M. Phillips and B. L. Davis, *J. Agr. Research*, **60**, 775 (1940).

[32] H. D. Weihe and M. Phillips, *J. Agr. Research*, **60**, 781 (1940).

[33] E. Anderson, J. Kesselman, and E. C. Bennett, *J. Biol. Chem.*, **140**, 563 (1941).

[34] W. G. Van Beckum and G. J. Ritter, *Paper Trade J.*, **105**, 127 (Oct. 28, 1937).

polyuronide hemicelluloses, but some losses occur when softwoods[35, 36] or straw[37] are delignified by existing methods. Alkaline extraction is still necessary to put into solution the major portion of the hemicelluloses in a holocellulose preparation, so that the polysaccharides present are still likely to be of dual origin. However, a water-soluble fraction, which would probably not be contaminated with cellulosan, can be obtained,[16] and much of the alkali-soluble material can be taken off by mild methods that would not produce so extensive an attack on the cellulosans as ordinarily occurs. The possibilities of this approach justify further study, particularly in the direction of seeking extracting agents that will bring the polyuronide hemicelluloses into solution without concurrent removal of cellulosan.

The preparation of cellulosans in a pure condition is a matter of no great difficulty. The starting material in this case is the cellulose fraction isolated from the plant material by the well-known Cross and Bevan method or one of its modifications that employs only neutral reagents. For laboratory-scale preparations, chlorination by hypochlorite may be substituted for chlorination by chlorine gas.[38] Pulps obtained by ordinary commercial pulping methods may also be employed, though it must be remembered that some loss of cellulosan has already occurred by hydrolysis. The cellulosan may be extracted by treatment with hot alkali, and the amount removed will depend on the time and temperature of treatment.[39] Purification can be carried out by precipitation with copper as described above, and products so obtained have been found to consist almost solely of xylan, even though in the original extract glucosan must have been present.[40] Preparations from gymnosperm celluloses in which mannan also is present have not been described.

4. Composition and Structure

The constitutional chemistry of the hemicelluloses, particularly the polyuronide hemicelluloses, is in a highly unsatisfactory state. Probably the best that can be said is that there is some general information as to the nature of the constituent groups involved in hemicelluloses from a considerable number of different sources. It is likely that all hemicellulose

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[35] W. G. Van Beckum and G. J. Ritter, *Paper Trade J.*, **108**, 27 (Feb. 16, 1939).
[36] C. V. Holmberg and E. C. Jahn, *Paper Trade J.*, **111**, 33 (July 4, 1940).
[37] W. A. Schenck and E. F. Kurth, *Ind. Eng. Chem.*, **33**, 1398 (1941).
[38] A. G. Norman and S. H. Jenkins, *Biochem. J.*, **27**, 818 (1933).
[39] A. G. Norman, *Biochem. J.*, **30**, 2054 (1936).
[40] W. N. Haworth, E. L. Hirst, and E. Oliver, *J. Chem. Soc.* **1934**, 1917.

preparations so far obtained have been mixtures, but there is, in fact, reason for believing that the methods of separation and fractionation that have been rather generally used may have given a spuriously complex picture. That is not to say that there is one polyuronide hemicellulose common to all plant materials, or even that there is one typical polyuronide hemicellulose in any particular plant material, because preparations of widely different specific rotations have been described from the same source, but to say that separation by differential precipitation does not necessarily accomplish separation into chemical entities. The major separation ordinarily employed in one form or another distinguishes only between the less-soluble and more-soluble fractions. Hemicellulose A preparations represent those polysaccharides easily precipitated, and B and/or C preparations consist of those fractions that are presumably of smaller molecular dimensions for the precipitation of which the addition of alcohol or acetone is necessary. Polysaccharides usually have a chain structure, but there is the possibility that one polysaccharide existing as molecules of different chain length could appear in all fractions. Similarly if the polysaccharide had a branched chain like some of the plant gums, separation by physical means might again give fractions that did not differ with respect to the amounts of the several components present. It is only likely, therefore, that the system of differential precipitation now used will give chemically distinct fractions if it happens that these differences are also clearly correlated with differences in molecular size. In general the more-soluble fractions appear to have a higher uronic content than the less-soluble fractions. For example, the respective contents of methoxyhexuronic acid in the most-soluble and least-soluble fractions from black locust sapwood were 12.10% and 7.92%, respectively, or from lemonwood 15.93% and 9.50%.[41] Such a difference cannot be regarded as evidence of efficiency in separation, however, because another explanation is possible. As mentioned earlier, most workers have consistently ignored the cellulosan in fractionating hemicellulose extracts. It has been established by extraction from isolated cellulose, free of polyuronide hemicelluloses, that the cellulosans are simple polysaccharides containing one constituent group only. The most widespread cellulosan is undoubtedly xylan. Though homogeneous as far as constituent groups are concerned, the cellulosans are most unlikely to be uniform in respect to chain length. If put through the fractionation system applied to hemicellulose extracts, xylan, at least, appears predominantly in the less-soluble fractions, but by no means exclusively so.

[41] E. Anderson, M. Seeley, W. T. Stewart, J. C. Redd, and D. Westerbeke, *J. Biol. Chem.*, **135**, 189 (1940).

There is, therefore, the real possibility that differences in uronic content and other groups between the less-soluble and more-soluble fractions precipitated from an alkaline extract may be due in part to decreasing amounts of cellulosan precipitated along with the polyuronide hemicelluloses as the alcohol concentration is raised. This explanation is supported by an examination of the analyses obtained on the hemicellulose extracted from white pine,[33] the cellulosan fraction of which would contain both mannan and xylan. Mannan appeared in all fractions, and indeed these authors recognized the presence of "a mannan free of a uronic acid." They also presumed mannose units to be present in the truly polyuronide fraction, but the published evidence does not make clear how it was established that this was the case, or that simple mixture was not involved.

From a wide range of plant materials, mostly lignified, preparations have been obtained that appeared to consist of xylose and monomethoxyglucuronic acid in proportions varying from 6 to 12 or more xylose units per hexuronic group. The methoxyl group is extremely stable and resists treatment with both acid or alkali. Hydrolysis of such preparations yields a stable aldobionic acid consisting of one xylose group linked to methoxyhexuronic acid. Long boiling with acid fails to resolve such an acid into its constituent units.[42] Acids containing two pentose units linked to one methoxyhexuronic acid group have also been obtained.[33] These have contained only one reducing group and therefore are probably the terminal units of a straight chain.

Some hemicellulose preparations give a blue, violet, or bluish-green color with dilute iodine solution which may be discharged by heating or destroyed by treatment with takadiastase.[43] O'Dwyer[44] showed that the blue color reaction which was given by the hemicellulose A fraction from oak sapwood but not by the same fraction from the heartwood was due to the presence of anhydroglucose units attached to the molecule. Sapwood hemicellulose A, when freed from these glucose residues by enzyme digestion or mild acid hydrolysis, seemed chemically almost identical with the heartwood product. The recurring unit of the heartwood product seemed to consist of eleven xylose units per methoxyhexuronic acid group, whereas the sapwood product contained in addition one glucose unit. From both, on prolonged digestion with takadiastase, was obtained a soluble polysaccharide, the analysis of which corresponded closely to the requirements of six xylose units per methoxyhexuronic acid. A product of similar properties

[42] E. Anderson and S. Kinsman, *J. Biol Chem.*, **94**, 39 (1931).
[43] M. H. O'Dwyer, *Biochem. J.*, **28**, 2116 (1934).
[44] M. H. O'Dwyer, *Biochem. J.*, **33**, 713 (1939); **34**, 149 (1940).

and composition was obtained by identical means from the hemicellulose B preparations from the same source, and it was clear that no fundamental differences existed between the A and B fractions from the different parts of the wood. About 60% or more of all preparations could be accounted for by assuming a recurrent nucleus of six xylose units per methoxyhexuronic group, and constitutional differences between the various preparations seemed confined to the remaining part of the molecule. The presence of anhydroglucose units in some hemicellulose preparations has been taken as an indication that starch is the precursor. The glucosan-containing hemicelluloses are regarded as transitional between starch or dextrin on the one hand and a stable xylan-glucuronide on the other.

Results similar to those of O'Dwyer have been obtained in studies of other hardwoods,[45] though higher proportions of xylose to uronic acid have been reported.[14, 41] From less highly lignified sources such as corncobs,[29] cottonseed hulls,[46] hop flowers,[47] oat hulls,[48] wheat straw,[32] sugar cane bagasse,[49] and alfalfa hay,[31] similar preparations have been obtained, some of which have been less extensively studied, but all of which have consisted predominantly of xylose units linked to a methoxyuronic acid.

Because of the virtual certainty discussed above that all these preparations contained some xylan not combined but concurrently extracted from the cellulose, the uronic content of the true polyuronide fraction is likely to be considerably higher, or at least the proportion of xylose to uronic groups to be lower. That this is highly probable may be seen from the work of Mitchell and Ritter,[16] who from maple holocellulose obtained hemicellulose fractions that, because of the mild means of extraction employed, would be unlikely to contain xylan from the cellulose. Preparations removed by hot water and dilute sodium carbonate contained approximately three xylose groups per uronic unit. When more drastic extracting agents were used (cold 4% and hot 10% sodium hydroxide), the proportions increased to roughly 8 and 10, respectively. The fractions extracted by water and carbonate represented, however, only about 25% of the material extracted. It would be of great interest to have further comparative studies of the hemicelluloses extracted by this procedure and concurrently from two or three sources by the conventional methods. Another feature of the work on maple holocellulose was the observation that the

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[45] L. Sands and W. T. Gary, *J. Biol. Chem.*, **101**, 573 (1933).
[46] E. Anderson, J. Hechtman, and M. Seeley, *J. Biol. Chem.*, **126**, 175 (1938).
[47] S. Angell and F. W. Norris, *Biochem. J.*, **30**, 2159 (1936).
[48] P. W. Krznarish, *Cereal Chem.*, **17**, 457 (1940).
[49] B. L. Davis and M. Phillips, *J. Agr. Research*, **63**, 241 (1941)

hemicelluloses may have acetyl groups normally linked to them. Approximately 9% acetyl was found in the water-soluble fractions, and this, of course, would ordinarily be missed if alkaline extractions were employed.

Although the majority of the hemicelluloses studied recently have been of the xylan-glucuronide type, preparations from nonlignified sources have been found to contain arabinose, galactose, and galacturonic acid. Buston[10] has suggested that this is characteristically the case, but insufficient studies have been made to permit of such a generalization. In preparations from certain grasses, leaves, and pods,[9, 10] galactose has been the preponderant constituent.

The structure of the polyuronide hemicelluloses is, therefore, far from clear. There are indications of a chain molecule terminated by a hexuronic group, and the possibility exists that the chain may be branched, as in the gums. The chief evidence for the latter statement, however, lies in differences in hydrolysis rates that could also be accounted for by admixture with cellulosan. Undoubtedly, considerable variation exists in molecular size, and it is questionable whether the molecules isolated are representative of the original molecules in the cell wall. Reduction in molecular size may occur as in pectin without any change in composition. The suggestion has been made that the carboxyl group of one molecule forms an ester linkage with a hydroxyl on another, building up in this way a long multiple chain that would be resolved by treatment with alkali.[33] The noncarboxyl end of such chains might be linked glycosidically to glucosan or lignin or other materials. It has to be admitted that this is largely speculative, and that little progress can be expected until well-defined hemicellulose preparations can be submitted to the rigorous techniques of the constitutional carbohydrate chemist.

C. PECTIN[50]

The pectic substances are found in all young plant tissues and are characteristic constituents of fruits and fleshy roots. In tissues that become lignified and in which secondary thickening of the cell wall takes place, the pectic content rapidly diminishes, though some calcium or calcium-magnesium pectate may persist to maturity in the middle lamella and can be isolated from mature wood.[51] In contrast to the relatively low uronic content of the hemicelluloses, the pectic substances have long been recognized as being predominantly polyuronide in nature, and are now consid-

[50] A more detailed treatment of this topic may be found in A. G. Norman, *Ann. Rev. Biochem.*, **10**, 76 (1941).

[51] E. Anderson, *J. Biol. Chem.*, **112**, 531 (1936)

ered to consist almost exclusively of galacturonic units. Most of the carboxyl groups of the pectin molecule *in situ* are esterified. Two methoxylated forms are found, differing in solubility, possibly only for reasons connected with chain length or degree of molecular aggregation, though other theories have been advanced. Protopectin is insoluble in water but may be removed from the cell wall of unlignified tissues by extraction with hot dilute acids, such as 0.5% oxalic acid, or even 0.5% ammonium oxalate. It is undoubtedly the precursor of the water-soluble modification, known as pectin, that occurs particularly in fruits and is formed enzymatically in the process of ripening and senescence. Protopectin was believed by some to be a pectin-cellulose complex (pectocellulose) but the evidence in favor of such a view is far from strong and the theory is hardly compatible with present-day ideas as to the molecular structure of either cellulose or pectin. In this connection, it should be mentioned that in at least one case,[52] the pectic substances of the cottonseed hair, the insolubility is due to the presence of bound calcium and other polyvalent metal ions.

In the case of pectin preparations, as with other cell-wall polysaccharides, criteria of purity are lacking. Extraction may be carried out by comparatively mild methods, but the products obtained vary in galacturonide content, in viscosity, and in the ability to form jellies with sugar and acid. The crude preparations obtained by many workers and by various methods usually contain about 70 to 80% galacturonide, the remainder of the preparation being accounted for by arabinose and galactose units. By treatment with dilute alkali or dilute acid, the galacturonide content of the preparations can be caused to rise, and indeed a substantially pure polygalacturonide can be obtained by such means. Such products, however, often have much reduced viscosity and jellying power which are characteristics of molecular disaggregation or reduced molecular size. Accordingly, for some time the pectin molecule was believed to consist of a galacturonide to which was linked arabinose and galactose in the proportions of approximately 4:1:1, it being recognized that the attachment of the sugar units might differ somewhat from that between the uronic groups to account for their susceptibility to mild hydrolysis. This theory is now, however, being abandoned in favor of the view that the pectin molecule is essentially a long-chain polygalacturonide with which may be associated pure araban and galactan. The relative proportions of each ordinarily present seem to be rather uniform, but it is by no means certain that they are closely related sterically. The araban from apple pectin was said to be composed of

[52] R. L Whistler, A. R. Martin, and M. Harris, *J. Research Natl. Bur. Standards*, **24**, 555 (1940).

furanose units and to be probably of the alpha-configuration.[53] It could not be formed by simple decarboxylation of a polygalacturonide, the units of which are of the pyranose form.[54, 55] A long-chain molecular structure for pectin was deduced from osmotic pressure, viscosity, and x-ray studies on the dinitro derivative, and values of from 30,000 to 100,000 were obtained for the molecular weight.[56, 57, 58] Short-chain fragments of 8 to 13 units have been obtained by treatment of pectic acid with dry methanol and hydrochloric acid[59] or by complete methylation.[54] The high viscosity of pectin in solution is regarded as additional evidence of large molecular dimensions. However, some form of branched structure may be present, since accompanying the decrease in viscosity of an enzymatically hydrolyzed pectin solution there is not as large an increase in reducing power as would be expected if long straight chains were being broken.[60] The physical chemistry of pectin is particularly difficult because the pectin molecule, the dimensions of which apparently may vary enormously, has also the peculiarity of having a variable equivalent weight depending upon the degree of esterification with methyl groups.

The observation that the pectic substances decrease in proportion to other cell-wall constituents as plant tissues mature has led to the suggestion that pectin may undergo transformation to hemicelluloses or lignin. Very little evidence in support of such theories has been adduced and indeed in the only attempt that has been made experimentally to test them,[10] the pectic substances have been found to possess a high degree of stability. In any case, if pectin is decarboxylated to give a hemicellulose, the products could only be of the galacturonoaraban type so that such a change could not be used to account for the xylan-glucuronide hemicelluloses which seem to occur most commonly in lignified tissues. Moreover, it is probable that a different type of linkage may be involved, since the polygalacturonide of pectin is unusually sensitive to the action of hot dilute alkalies, whereas hemicellulose groupings seem relatively resistant. A knowledge of whether the linkage between constituent units of the polyuronide hemicelluloses is of the alpha-type as in starch or pectin, or the beta-type as in cellulose, would help in arriving at a decision as to possible precursors and transformations.

[53] E. L. Hirst and J. K. N. Jones, *J. Chem. Soc.*, **1939**, 454.
[54] S. Luckett and F. Smith, *J. Chem. Soc.*, **1940**, 1106.
[55] G. H. Beavan and J. K. N. Jones, *Chemistry & Industry*, **17**, 363 (1939).
[56] F. A. Henglein and G. Schneider, *Ber.*, **69B**, 309 (1936).
[57] G. Schneider and M. Ziervogel, *Ber.*, **69B**, 2530 (1936).
[58] G. Schneider and U. Fritschi, *Ber.*, **69B**, 2537 (1936).
[59] S. Morell, L. Baur, and K. P. Link, *J. Biol. Chem.*, **105**, 1 (1934).
[60] Z. I. Kertesz, *J. Am. Chem. Soc.*, **61**, 2544 (1939).

Chapter V

LIGNIN AND OTHER NONCARBOHYDRATES

LIGNIN AND OTHER NONCARBOHYDRATES

F. E. Brauns

A. OCCURRENCE, DETERMINATION, AND PHYSICAL PROPERTIES OF LIGNIN

1. Occurrence

Cellulose occurs in nature in a relatively pure state only in seed hairs. In wood and straw it is associated with hemicelluloses and polyuronides in addition to noncarbohydrate materials which consist chiefly of lignin together with small amounts of tannins, resins, fats, and other minor components. The lignin in wood is chiefly located in the middle lamella and in the cell wall, from which it can be separated by saccharification of the carbohydrate material with strong mineral acids. Lignin, therefore, can be defined as that part of the wood or straw which remains as an insoluble product when those substances, after previous removal of the tannins, resins, fats, etc., by suitable extraction, are treated with strong mineral acids. It should be emphasized that lignin is not just an insoluble residue; it is differentiated from the remaining constituents of wood and is characterized by the fact that a large portion of it is made up of methoxylated aromatic residues and is, therefore, quite different from the carbohydrate portion of the plant cell wall. Furthermore, at least a sizable proportion of the lignin in hardwood is structurally different from the lignin in coniferous woods, while very little is known with certainty of the relation of lignin in straw to the lignin in wood. The origin of lignin is still unknown, although there has been much speculation as to the possibility of its being derived from carbohydrates.

The study of lignin is rendered extremely difficult by its physical and chemical properties. It is easily changed by chemicals and is, therefore, difficult to isolate in an unchanged state by processes involving the use of these reagents. Isolated lignin is generally an amorphous material with a high average molecular weight and, like so many natural polymers, is probably not uniform. Hilpert,[1] on the basis of investigations with

[1] R. S. Hilpert and H. Hellwage, *Ber.*, **68B**, 380 (1935); R. S. Hilpert, *Cellulosechem.*, **17**, 25 (1936).

beechwood and straw, even claims that there is no basic difference between lignin and the carbohydrates, and that lignin is a secondary reaction product formed by the action of mineral acid on reactive, partly methylated carbohydrates. The question as to whether lignin is present in lignified material in a free state or is combined with other constituents is still open to discussion, although in recent years more and more lignin chemists are of the opinion that at least the major part of the lignin is combined with carbohydrate material, probably with hemicelluloses through a glycosidic (hemiacetal?) linkage.[2–6] (See also Chapter II, E.) Enzymes split off only a part of the carbohydrate, a complete fission being achieved only by an acid hydrolysis. A small percentage of the lignin in coniferous woods, and probably also in deciduous woods, is in a free state and is soluble in suitable solvents, such as alcohol or dioxane. The material thus isolated in the unchanged state is called "native lignin."[7] The major part of the lignin, however, can be isolated only by the use of more drastic reagents which undoubtedly modify the lignin at the same time.[8]

2. Color Reactions

Lignin can be detected in lignified material by certain color reactions with amines and phenols,[9] of which the one using phloroglucinol and hydrochloric acid is the best known. In this reaction a bright purple color is obtained. It is admitted that this color reaction is not specific for lignin, as some aldehydes, for example, coniferyl aldehyde, give similar colorations. For this reason it has been claimed recently[10] that this coloration is due, not to lignin, but to the presence of aldehydes, particularly vanillin and coniferyl aldehyde. While this may be in part the case, isolated native lignin which, because of the method of isolation and purification, is free of such aldehydes, gives the same bright purple color reaction.[7] When sprucewood or isolated spruce native lignin is completely methylated in regard to diazomethane, it no longer gives the color reaction. This indi-

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[2] P. Klason, *Ber.*, **56B**, 300 (1923).
[3] M. Phillips, *J. Am. Chem. Soc.*, **50**, 1986 (1928).
[4] F. E. Brauns and D. S. Brown, *Ind. Eng. Chem.*, **30**, 779 (1938).
[5] T. Ploetz, *Ber.*, **73B**, 74, 790 (1940).
[6] A. J. Bailey, *Paper Trade J.*, **110**, 29 (Jan. 4, 1940).
[7] F. E. Brauns, *J. Am. Chem. Soc.*, **61**, 2120 (1939).
[8] T. Ploetz, *Ber.*, **72B**, 1885 (1939).
[9] M. Phillips, *Chem. Revs.*, **14**, 103 (1934).
[10] K. Wiechert, *Papier-Fabr.*, **37**, Tech.-wiss. Tl., 17, 30 (1939).

cates that the group responsible for the reaction has been methylated by this reagent. The Mäule reaction,[11] in which the lignified material is treated successively with potassium permanganate solution, dilute hydrochloric acid, and ammonium hydroxide to give a brilliant red color, seems to be a specific lignin reaction for deciduous woods, but coniferous woods give only an indefinite brownish color under these conditions.

3. Quantitative Determination

Numerous methods have been proposed for the quantitative determination of lignin,[9] the most common one being based upon the use of 72% sulfuric acid as outlined by the Forest Products Laboratory in Madison, Wisconsin. This method is suitable for coniferous woods but not for deciduous woods.[12, 13] It may also be used for pulps.[14] If a lignin from a sulfite or kraft pulp is to be analyzed further for sulfur, fuming hydrochloric acid as proposed by Willstätter should be applied for the lignin isolation. Since, however, the residual lignin in chemical pulps has been chemically changed,[14, 15] further work is necessary to determine to what extent this change affects the true lignin content.

As already mentioned, the major part of the lignin in lignified material can be isolated only by drastic reactions. Whatever method is used, it is important that the finely ground plant material first be extracted with an alcohol-benzene mixture (1:2) to remove the resins, fats, waxes, and volatile oils, and then with water to remove sugars and other water-soluble material. In some cases, for example with hardwoods and straws, an extraction with dilute aqueous sodium hydroxide may be advisable for the removal of tannins, pectins, and other gummy substances, as they may contaminate the lignin. Such a treatment must be carried out in the absence of air.[16–19]

4. Physical Properties

Lignin obtained by removal of the cellulose still has the morphological structure of the cell and shows double refraction.[18] It is insoluble in or-

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[11] C. Mäule, *Beitr. Z. wiss. Botan.*, **4**, 166 (1900).
[12] F. E. Brauns, *Paper Trade J.*, **111**, 33 (Oct. 3, 1940).
[13] K. Freudenberg and T. Ploetz, *Ber.*, **73B**, 754 (1940).
[14] L. L. Larson, *Tech. Assoc. Papers*, Ser. **24**, 243 (1941).
[15] C. E. Ahlm, *Paper Trade J.*, **113**, 115 (Sept. 25, 1941).
[16] A. Friedrich and J. Diwald, *Monatsh.*, **46**, 31 (1925).
[17] K. Freudenberg, M. Harder, and L. Markert, *Ber.*, **61B**, 1762 (1928).
[18] K. Freudenberg, H. Zocher, and W. Dürr, *Ber.*, **62B**, 1814 (1929).
[19] H. Hibbert and E. G. King, *Can. J. Research*, **14B**, 12 (1936).

ganic solvents and is light to dark brown in color, depending upon the mod
of isolation. Its refractive index is 1.61.[18, 20] The layer thickness of ligni

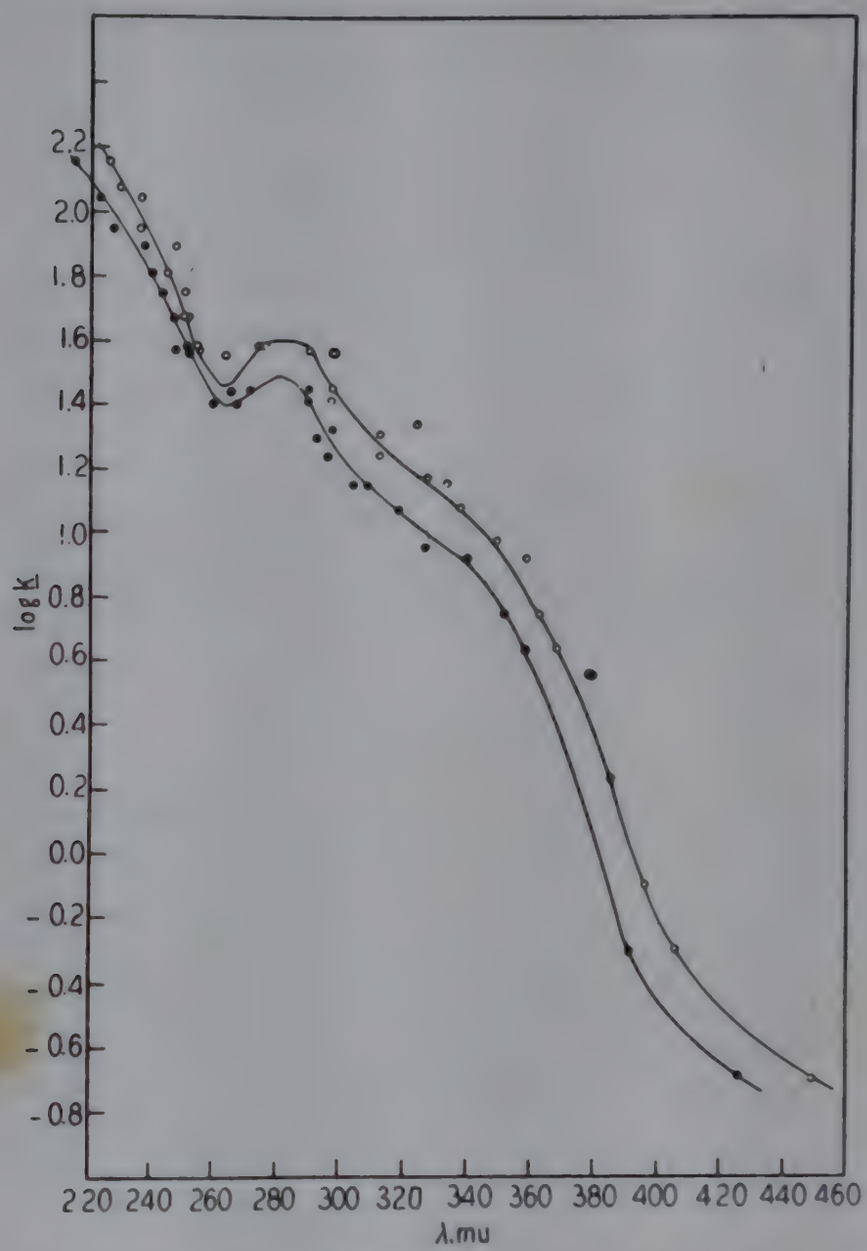

FIG. 1.—ABSORPTION SPECTRA OF NATIVE LIGNIN AND ACETYLATED NATIVE LIGNIN (GLADING[21]).

Solvent, 90% dioxane.

—○— Native lignin.

—●— Acetylated native lignin.

determined by spreading experiments with sodium lignoazobenzene
sulfonate is 20 Å., indicating a three-dimensional structure.[20] X-ra

[20] K. Freudenberg, W. Belz, and C. Niemann, *Ber.*, **62B**, 1554 (1929); K. Freudenberg
F. Sohns, W. Dürr, and C. Niemann, *Cellulosechem.*, **12**, 263 (1931).

[21] R. E. Glading, *Paper Trade J.*, **111**, 32 (Dec. 5, 1940).

analysis shows it to be amorphous.[22] It is optically inactive.[23] The position and intensity of its spectral absorption bands indicate its aromatic character[21, 24, 25] (see Fig. 1). Isolated amorphous lignin is of high molecular weight.[26] Isolated spruce native lignin is almost white; its solution in dioxane, however, is reddish brown.[7] For the lignin building unit discussed below, a molecular weight of 840 has been calculated,[7, 27] which means that it is composed of five phenylpropane lignin building stones, each of molecular weight 170. There is little doubt that lignin is built according to a definite pattern from building stones belonging to a group of biochemically related types.

B. ISOLATION OF LIGNIN

1. Laboratory Procedures

The methods for the isolation of lignin may be divided into two main classes: those in which the lignin is obtained as an insoluble residue after removal of the other components by hydrolysis; and those in which the lignin is dissolved, leaving a residue of cellulose and other carbohydrates. In both cases the lignin undergoes more or less drastic changes. Reagents in the first class which are used to hydrolyze the carbohydrate material include 64–72% sulfuric acid,[28] fuming hydrochloric acid,[29, 30] hydrogen fluoride,[30a] or mixtures of these acids.[31, 32] The original methods have been modified in many ways. Still another method of dissolving the carbohydrate material is that conceived by Freudenberg,[17] who extracted the cellulose and other carbohydrates from wood by means of cuprammonium solution after a preliminary hydrolysis with boiling 1% sulfuric acid or 7% oxalic acid. After several such alternate treatments, a lignin having

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[22] E. Wedekind and J. R. Katz, *Ber.*, **62B**, 1172 (1929).
[23] K. Freudenberg and F. Sohns, *Ber.*, **66B**, 262 (1933).
[24] R. O. Herzog and A. Hillmer, *Ber.*, **60B**, 365, 1600 (1927); **64B**, 1288 (1931).
[25] E. Hägglund and E. W. Klingstedt, *Svensk Kem. Tid.*, **41**, 185 (1929); *Z. physik. Chem.*, **A152**, 295 (1931).
[26] D. L. Loughborough and A. J. Stamm, *J. Phys. Chem.*, **40**, 1113 (1936).
[27] P. B. Sarkar, *J. Indian Chem. Soc.*, **11**, 691 (1934).
[28] P. Klason, *Cellulosechem.*, **4**, 81 (1923); **12**, 36 (1931).
[29] R. Willstätter and L. Kalb, *Ber.*, **55B**, 2637 (1922).
[30] L. Kalb and T. Lieser, *Ber.*, **61B**, 1007 (1928).
[30a] K. Wiechert, *Cellulosechem.*, **18**, 57 (1940); see also ref. 10, p. 450.
[31] H. Urban, *Cellulosechem.*, **7**, 73 (1926).
[32] K. Freudenberg and M. Harder, *Ber.*, **60B**, 581 (1927).

a light-brown color is obtained. The above lignin preparations are insoluble in any organic solvent, and this, of course, affects their use for further investigation.

The methods of the second class comprise those using organic reagents on the one hand, and inorganic on the other, or both. Klason[33] first used an organic reagent; he extracted the lignin from sprucewood by refluxing the wood for 6 to 10 hours with ethanol containing 5% hydrochloric acid. The lignin was isolated from the solution by distillation of the alcohol. Similar reactions have been applied by many other lignin chemists, with various monohydroxy and polyhydroxy alcohols, such as methanol,[34] ethanol,[16, 35–38] butanol,[39] isobutanol,[40] amyl alcohol,[40] ethylene glycol,[41–45] glycol monomethyl ether,[45, 46] chloroethylene glycol,[43] and glycerol α-monochlorohydrin,[47] and monoethanolamine.[48] In the case of the monohydroxy alcohols, Hägglund[40] suggested, as early as 1928, that the lignin combines with the alcohol, forming a hemiacetal. It has been experimentally proved that spruce native lignin reacts with methanol in the presence of hydrochloric acid with the formation of a methanol lignin having two new methoxyl groups.[7] On treatment with 72% sulfuric acid these groups are split off, indicating the possibility of an acetal-like linkage. Under similar conditions, butanol lignin loses the butanol groups.[39] Since the alcohol lignins are insoluble in dilute mineral acids, the original lignin cannot be regenerated from the acetal form without being changed. Carefully purified dioxane in the presence of hydrochloric acid will not dissolve lignin,[49] despite

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[33] P. Klason, *Tek. Tid.*, **23**, Uppl. C, 55 (1893).

[34] F. E. Brauns and H. Hibbert, *Can. J. Research*, **13B**, 28 (1935).

[35] J. Grüss, *Ber. deut. botan. Ges.*, **38**, 361 (1920); **41**, 48 (1923).

[36] A. Friedrich and B. Brüda, *Monatsh.*, **46**, 600 (1925).

[37] B. Holmberg and S. Runius, *Svensk Kem. Tid.*, **37**, 189 (1925).

[38] H. Hibbert and coworkers, *J. Am. Chem. Soc.*, **60**, 2815 (1938); **61**, 516, 868, 2196, 2198 (1939); **62**, 2803 (1940).

[39] H. Charbonnier, *Paper Trade J.*, **114**, 31 (Mar. 12, 1942).

[40] E. Hägglund and H. Urban, *Cellulosechem.*, **8**, 69 (1927); **9**, 49 (1928).

[41] H. Gabriel, Dissertation, Leipzig, 1928.

[42] B. Rassow and H. Gabriel, *Cellulosechem.*, **12**, 227, 290, 318 (1931).

[43] H. Hibbert and coworkers, *Can. J. Research*, **2B**, 357, 364 (1930); **3B**, 130 (1930).

[44] B. Rassow and R. Lüde, *Z. angew. Chem.*, **44**, 827 (1931).

[45] K. R. Gray, E. G. King, F. E. Brauns, and H. Hibbert, *Can. J. Research*, **13B**, 35 (1935).

[46] W. Fuchs, *Ber.*, **62B**, 2125 (1929).

[47] H. Hibbert and J. B. Phillips, *Can. J. Research*, **3B**, 65 (1930).

[48] J. D. Reid, E. C. Dryden, and S. I. Aronovsky, *Paper Trade J.*, **113**, 27 (Aug. 14, 1941).

the fact that a patent[50] has been issued for this process. (Apparently a dioxane-containing glycol or acetal was used.[49])

Although the extraction of wood with alcohol removes only a part of the lignin, phenol will dissolve the lignin almost quantitatively. The use of this reaction commercially, however, has failed to materialize as the cellulose remaining is of poor quality due to the high temperatures required in the absence of catalysts (180–200°C.)[51] or to the action of hydrochloric acid when it is used as a catalyst.[52–55] In the presence of the catalyst, reaction is complete after heating at 95–100°C. for half an hour. The lignin can be isolated from the filtered phenol solution by distilling off the excess phenol and precipitating the main part of the phenol lignin with ether. From the mother liquor, an ether-soluble phenol lignin can be isolated.[55] In both phenol lignins a large amount of phenol has reacted with the lignin. Substituted phenols also dissolve lignin to a considerable extent.[53] Fuchs[56] has shown that the phenol may be split from the phenol lignin by the action of a mixture of acetic and hydrobromic acids but at the same time the lignin molecule itself is also attacked.

The mechanism of the reaction between phenols and lignin is not yet clear, nor has it been clarified by the substitution of thiophenol, as this reaction is still more complicated. Holmberg[57] first showed that thio compounds are especially reactive with lignin. Benzyl mercaptan and thioglycolic acid, in the presence of small amounts of hydrochloric acid, react very easily with lignin, forming soluble lignin derivatives, which are very light in color as is also the resulting pulp.[58] These reactions appear at the moment to have no commercial applications.

2. Pulping Processes

Most technical methods for the dissolution of lignin involve the use of inorganic reagents. Since these operations are discussed in Chapter VI,

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[49] K. Freudenberg, *Tannin, Cellulose, Lignin.* J. Springer, Berlin, 1933, p. 125.

[50] O. Engel and E. Wedekind, German Patent 581,806 (Aug. 3, 1933); see also K. Storch, *Cellulosechem.*, **17**, 49 (1936).

[51] F. Bühler, German Patent 94,467 (1897).

[52] L. Kalb and V. Schöller, *Cellulosechem.*, **4**, 37 (1923).

[53] A. Hillmer, *Cellulosechem.*, **6**, 169 (1925).

[54] E. Wedekind, O. Engel, K. Storch, and L. Tauber, *Cellulosechem.*, **12**, 168 (1931).

[55] I. K. Buckland, F. E. Brauns, and H. Hibbert, *Can. J. Research*, **13B**, 61 (1935).

[56] W. Fuchs, *J. Am. Chem. Soc.*, **58**, 675 (1936).

[57] B. Holmberg, *Ing. Vetenskaps Akad. Handl.*, No. 103 (1930); No. 131 (1934).

[58] C. E. Ahlm and F. E. Brauns, *J. Am. Chem. Soc.*, **61**, 277 (1939).

only the mechanism of the reaction taking place between the reagents and the lignin, and the isolation of the lignin products will be discussed here. The three principal pulping procedures are the sulfite, the sulfate, and the soda processes.

(a) *Lignosulfonic Acid*

In the sulfite process, the lignin in the wood is dissolved by digesting chips with an acid calcium, magnesium, or sodium sulfite solution at an elevated temperature, whereby the lignin goes into solution as a salt of lignosulfonic acid; hydrolyzed carbohydrates are also present in the solution. Numerous methods for the isolation of the sulfonated lignin from the waste liquors have been suggested. They mostly involve precipitation by sodium chloride,[59, 60] calcium chloride,[61] mineral acids,[62] lime water,[63] basic lead acetate,[64] or organic bases,[65, 66, 67] decomposition of the precipitate, and further purification by dialysis. As the free lignosulfonic acid is quite unstable in its solid state,[64] its salts are usually used for research and technical processes.

According to Klason,[61] the sulfite waste liquor of a commercial cook contains two lignosulfonic acids; these are separated by precipitation of the alpha acid with β-naphthylamine hydrochloride, the beta acid remaining in solution. Lignosulfonic acid prepared under mild conditions does not contain the beta acid[66]; according to Hägglund,[68] the beta acid is formed from the alpha form during the treatment with bisulfite at a high temperature. The formation of lignosulfonic acid occurs in two stages: in the first the lignin is sulfonated with the formation of the solid lignosulfonic acid[69]; in the second the solid lignosulfonic acid is dissolved by an acid hydrolysis.[70] Several theories have been advanced for the actual reaction

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[59] K. H. A. Melander, *Cellulosechem.*, **2**, 41 (1921).

[60] W. Nippe and A. Ogait, *Cellulosechem.*, **11**, 38 (1930).

[61] P. Klason, *Arkiv Kemi, Mineral. Geol.*, **6**, No. 15 (1917).

[62] M. Hönig and J. Spitzer, *Monatsh.*, **39**, 1 (1918).

[63] G. C. Howard, *Ind. Eng. Chem.*, **26**, 614 (1934).

[64] E. G. King, F. E. Brauns, and H. Hibbert, *Can. J. Research*, **13B**, 88 (1935).

[65] P. Klason, *Ber.*, **53B**, 705, 1862, 1864 (1920).

[66] K. Freudenberg, F. Sohns, and A. Janson, *Ann.*, **518**, 62 (1935).

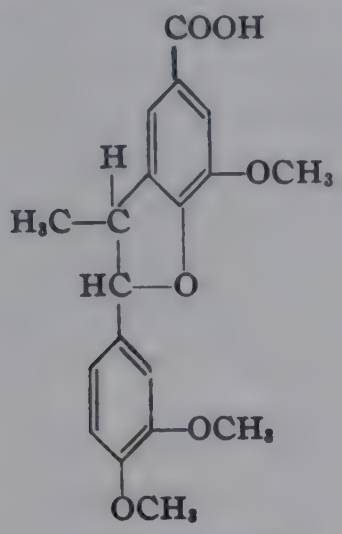
[67] W. Nippe, *Ber.*, **69B**, 1239 (1936).

[68] E. Hägglund, *Svensk Kem. Tid.*, **42**, 159 (1930).

[69] E. Hägglund, *Svensk Kem. Tid.*, **37**, 116 (1925); **38**, 177 (1926); E. Hägglund and T. Johnson, *Biochem. Z.*, **250**, 221 (1932).

[70] C. Kullgren and C. Du Rietz, *Svensk Kem. Tid.*, **42**, 179 (1930); **43**, 99, 161 (1931); **44**, 15 (1932); **45**, 185 (1933); **46**, 136 (1934); **49**, 52 (1937).

taking place between the lignin and the bisulfite. Klason[71] assumed that the sulfurous acid is added to an ethylenic bond in the lignin molecule; however, the presence of double bonds in isolated lignin has not been definitely established. Freudenberg[72] suggested that they are first formed during the sulfite cook by splitting off of water. In this case a hydroxyl group is removed and the lignosulfonic acid would have one hydroxyl group less than the original lignin. The opening of an ethylene oxide ring, as assumed by Klason,[73] or of a furan or pyran ring, as recently demonstrated by Freudenberg[74] on model experiments with Erdtman acid,



Erdtman Acid

would lead to the formation of a new phenolic hydroxyl group. Since, however, the number of methoxyl and hydroxyl groups is the same in lignosulfonic acid as in the original lignin in the wood,[23, 64, 75, 76] these reactions must be discarded. A sulfonation of the aromatic nucleus has been discussed by Freudenberg.[72] When sprucewood, methylated with diazomethane until the methoxyl content of its lignin is 21%, is subjected to a sulfite cook, the lignin is sulfonated but is not dissolved.[4, 77] Unlike isolated spruce native lignin, which is completely dissolved in a sulfite cook, its diazomethane-methylated derivative (having the same methoxyl content as the lignin in the diazomethane-methylated wood) is not dissolved.[7] In the methylated lignin the enolized carbonyl group is methylated, which

[71] P. Klason, *Ber.*, **53B**, 706 (1920).

[72] K. Freudenberg, *Tannin, Cellulose, Lignin*, p. 128; see ref. 49, p. 455.

[73] P. Klason, *Svensk Kem. Tid.*, **9**, 135 (1897).

[74] K. Freudenberg, M. Meister, and E. Flickinger, *Ber.*, **70B**, 500 (1937).

[75] E. Hägglund and G. E. Carlsson, *Biochem. Z.*, **257**, 467 (1933).

[76] E. Hägglund, *Holzchemie*. Akademische Verlagsgesellschaft m. b. H., Leipzig, 1939, p. 148.

[77] E. Hägglund, *Holzchemie*, p. 150; see ref. 76 above.

indicates that this group plays an important role in the sulfonation process.[12] It seems that the lowest sulfur content necessary for the dissolution of the lignin is 3.5%, which corresponds to one sulfonic group per lignin building unit.[12] As the residual lignin in a sulfite pulp is also sulfonated and on chlorination yields water-soluble decomposition products, this pulp is more easily bleachable than a kraft or soda pulp.

(*b*) *Thiolignin*

In the sulfate (kraft) process the lignin is rendered soluble by digesting the wood with a mixture of one part of sodium sulfide and two parts of sodium hydroxide in a 5% solution at 160–180°C. From the black liquor the lignin is thrown out, together with some hemicelluloses, by acidification with mineral acid, and is obtained, after purification, as a light-brown powder consisting of a mixture of thiolignin and alkali lignin.[15, 78, 79] The exact mechanism of the reaction between sodium sulfide and lignin is not yet known but there is little doubt that, because of partial hydrolysis of the sulfide, a mercapto group is formed in the lignin molecule.

(*c*) *Alkali Lignin*

In the soda process, in which only sodium hydroxide is used, a reaction similar to that occurring in the kraft process probably takes place. The alkali lignin, isolated from the black liquor of such cooks, has been the subject of various investigations,[80, 81] but the results vary widely, because the lignin is more or less drastically attacked by the alkaline cooking liquor and because black liquor obtained from commercial cooks has often been used for the preparation of the alkali lignin. In both the kraft and soda pulps the residual lignin is chemically changed.[15] Unlike lignosulfonic acid, both thiolignin and alkali lignin are insoluble in water and are precipitated from the alkali salt solutions by lime water. This may account in part for the difficulties involved in the bleaching of these pulps.

C. STRUCTURE OF LIGNIN

1. Elementary Composition

The elementary composition of lignin varies with its source and the method used for its isolation. Whereas the various isolated lignins run

[78] P. Klason and B. Segerfelt, *Arkiv Kemi, Mineral. Geol.*, **4**, No. 20 (1913).
[79] B. Holmberg and O. Anderzén, *Ber.*, **56B**, 2044 (1923).
[80] B. Holmberg and J. Wintzell, *Ber.*, **54B**, 2417 (1921).
[81] H. B. Marshall, F. E. Brauns, and H. Hibbert, *Can. J. Research*, **13B**, 103 (1935).

between 62.4 and 64.3% carbon and 5.4 and 6.0% hydrogen, isolated spruce native lignin has 63.6% carbon and 6.1% hydrogen.[7]

Two factors must be considered in attempting to elucidate the chemical nature of lignin: first, the characteristic groups which are present in lignin (analogous to glucose as the building stone of cellulose or to the various sugars and uronic acids characteristic of a gum); second, the molecular structure. The first of these points has been, to a considerable extent, answered by recent research on degradation by oxidation and by hydrogenation, which will be elaborated later in this chapter. It is now well established that lignin is built up almost entirely of building stones consisting essentially of an aromatic ring containing a three-carbon side chain, one or two methoxyls meta to this side chain, and an oxygen bridge or phenolic group para to the side chain. In addition, there may be carbon to carbon or carbon to oxygen bonds joining the aromatic ring to other portions of the structure. It appears that there are several types of bonds between the units in any sample of lignin.

For any final determination of the molecular structure it must be decided, therefore, whether there is some sort of a master unit which contains each of these modes of linkage, or whether the entities which go into solution, such as native lignin, lignosulfonic acid, phenol lignin, etc., differ from one another. They may be expected to differ, if they differ at all, in either molecular weight or internal structure. In the last analysis, a decision as to whether variations of these two types exist depends on the application of a fractionation technique which may be relied on to separate molecules if any differences exist between them. Such methods of fractionation have not been worked out for this particular problem. Fractionations that have been carried out[81a] have shown minor differences between fractions. However, as was shown above (see Chapter IV) in the case of hemicelluloses, inefficient fractionations may tend to indicate the presence of many components when there may be present only two or even one chief component and a difficultly separable impurity. Therefore, up to the present time more reliance has had to be placed on work with the unfractionated lignin, determining the number of functional groups and calculating the smallest molecule which would permit an integral number of these functional groups. There appears to be definite evidence for such a building unit[7, 27, 34] of molecular weight about 840 containing one enolic and one phenolic hydroxyl group. This structure may be considered a multiple of Freudenberg's phenylpropane lignin building stone in the same

[81a] R. F. Patterson, K. A. West, E. L. Lovell, W. L. Hawkins, and H. Hibbert, *J. Am. Chem. Soc.*, **63**, 2065 (1941).

sense as glucose is the building stone of cellobiose or maltose which, in turn, are the building units of cellulose and starch, respectively. The lignin building unit fulfills the requirements demanded by the experimental results such as methylation with diazomethane and with dimethyl sulfate, sulfonation, and formation of 6% acetic acid on oxidation with chromic acid and of 2.5% formaldehyde on distillation with 12% hydrochloric acid.

The concept of a lignin molecular weight of about 840 is useful as an aid for considering the relationships between the amounts of functional groups in lignin, and occasional use of this figure in the following discussion is, therefore, justified. A final decision as to the reality of such a molecule or building unit must await further work.

2. Aromatic Nature

The high carbon and low hydrogen contents of lignin indicate that it is either highly unsaturated or aromatic in character. Although the presence of double bonds in lignin is still open to discussion,[20, 82] there is definite proof of the presence of aromatic groups in lignin. On alkali fusion of spruce lignin, pyrocatechol (I) and protocatechuic acid (II) are obtained in various amounts depending upon the experimental conditions. In addition, some oxalic acid, formic acid, and carbon dioxide are formed.[17, 83] Beech lignin, under the same conditions, gives protocatechuic acid and gallic acid (III).[18] When spruce lignin is treated with sodium hydroxide at 165–170°C., methylated with dimethyl sulfate, and oxidized with potassium permanganate, veratric acid (IV), isohemipinic acid (V), dehydrodiveratric acid (VI), and traces of trimethylgallic acid (VII) are found.[84] Treatment of lignosulfonic acid with sodium hydroxide at 160°C.,[85, 86, 87] or of any lignin or lignin-containing material under the same conditions but in the presence of a mild oxidizing agent (such as nitrobenzene[88]), gives vanillin (VIII) up to 25% (based on the lignin). On similar treatment,

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[82] H. Hibbert and R. G. D. Moore, *Can. J. Research*, **14B**, 404 (1936).

[83] E. Heuser and A. Winsvold, *Cellulosechem.*, **2**, 113 (1921); **4**, 49, 62 (1923); *Ber.*, **56B**, 902 (1923).

[84] K. Freudenberg, A. Janson, E. Knopf, and A. Haag, *Ber.*, **69B**, 1415 (1936).

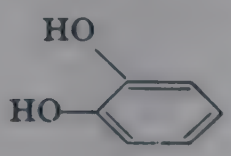
[85] K. Kürschner and W. Schramek, *Tech. Chem. Papier- u. Zellstoff-Fabr.*, **28**, 65 (1931); **29**, 35 (1932).

[86] G. H. Tomlinson and H. Hibbert, *J. Am. Chem. Soc.*, **58**, 345, 348 (1936).

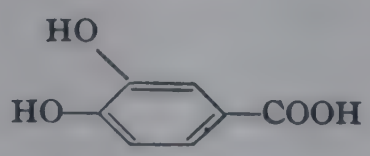
[87] E. Hägglund, *Svensk Papperstidn.*, **39**, 347 (1936); E. Hägglund and O. Alvfeldt, *Svensk Papperstidn.*, **40**, 236 (1937).

[88] K. Freudenberg, W. Lautsch, and K. Engler, *Ber.*, **73B**, 167 (1940).

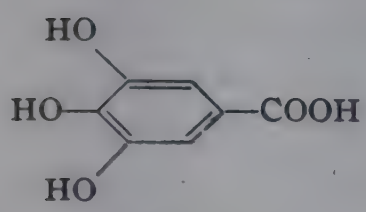
beech lignin gives syringaldehyde (IX).[89] On dry distillation of lignin, small amounts of eugenol, guaiacol, and vanillic acid are obtained.[90]



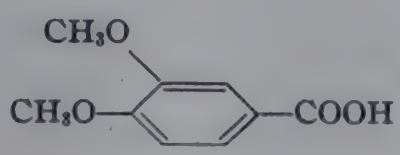
Pyrocatechol
I



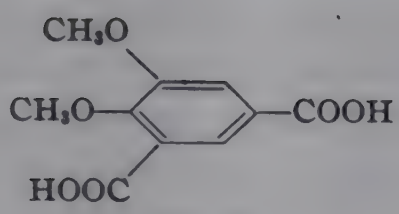
Protocatechuic Acid
II



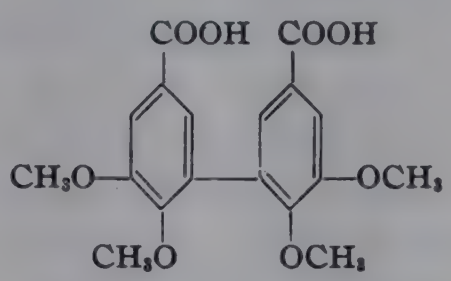
Gallic Acid
III



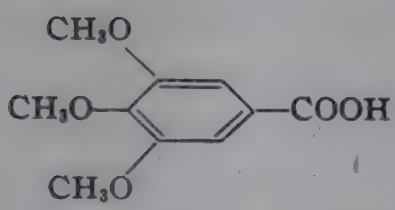
Veratric Acid
IV



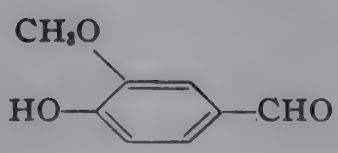
Isohemipinic Acid
V



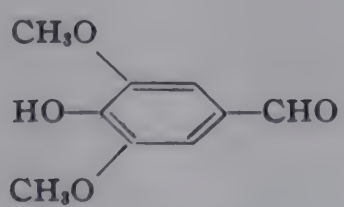
Dehydrodiveratric Acid
VI



Trimethylgallic Acid
VII



Vanillin
VIII



Syringaldehyde
IX

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[89] R. H. J. Creighton, J. L. McCarthy, and H. Hibbert, *J. Am. Chem. Soc.*, **63**, 312 (1941).

[90] B. Rassow and P. Zickmann, *J. prakt. Chem.*, **123**, 189 (1929).

3. Reactive Groups

Lignin contains a number of typical groups. The presence of aromatically bound methoxyl groups has been definitely established.[91] The methoxyl content of lignin from coniferous woods and straws is about 15% and that from deciduous woods is about 21.5%, varying somewhat with the method of isolation. Spruce native lignin has a methoxyl content of 14.8%[7, 92] which corresponds to four methoxyl groups per lignin building unit of a molecular weight of 840.[7] When carefully prepared spruce lignin is subjected to a distillation with 12% hydrochloric acid[17, 32] or 28% sulfuric acid,[27] up to 2.5% formaldehyde is split off; this is assumed to originate from a methylenedioxy group.[32, 93–95] While the absence of acetyl groups in native lignin has been definitely proved,[96] the presence of hydroxyl groups in lignin is shown by the fact that these can be acetylated and methylated; for each lignin building unit of spruce lignin, four hydroxyl and four methoxyl groups are indicated. At least one of the four hydroxyls is phenolic in character, because isolated spruce native lignin and certain lignin preparations, such as the alcohol lignins, are soluble in dilute alkali from which they are precipitated by carbon dioxide.[7, 34, 45] Likewise, the presence of a phenolic hydroxyl group has been definitely shown in lignosulfonic acid.[64] The other hydroxyl groups are aliphatic and probably secondary and tertiary in character.[66] The presence of a carbonyl group has been the subject of dispute for many years. As the lignins isolated by strong mineral acids are changed, it is not surprising that this group cannot be detected in these preparations.[97] In the alcohol lignins, the alcohol may have reacted with the carbonyl group to form acetals which prohibit its detection. Isolated spruce native lignin has one easily enolizable carbonyl group per lignin building unit[7]; on the other hand, spruce lignin isolated by formic acid is claimed to have a nonenolizable carbonyl group.[98] Carboxyl groups are not present in lignin.[99]

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[91] K. Freudenberg, W. Belz, and C. Niemann, *Ber.*, **62B**, 1554 (1929).

[92] E. Hägglund, *Holzchemie*, p. 199; see ref. 76, p. 457.

[93] E. Hägglund and coworkers, *Biochem. Z.*, **147**, 74 (1924); **179**, 376 (1927); **207**, 1 (1929).

[94] M. J. Hunter, G. F. Wright, and H. Hibbert, *Ber.*, **71B**, 734 (1938).

[95] K. Freudenberg, F. Klinck, E. Flickinger, and A. Sobek, *Ber.*, **72B**, 217 (1939).

[96] E. F. Kurth and G. J. Ritter, *J. Am. Chem. Soc.*, **56**, 2720 (1934).

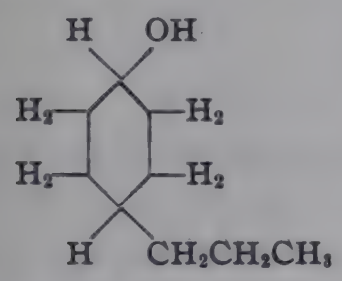
[97] E. Hägglund, T. Johnson, and L. H. Trygg, *Svensk Papperstidn.*, **32**, 815 (1929).

[98] G. F. Wright and H. Hibbert, *J. Am. Chem. Soc.*, **59**, 125 (1937).

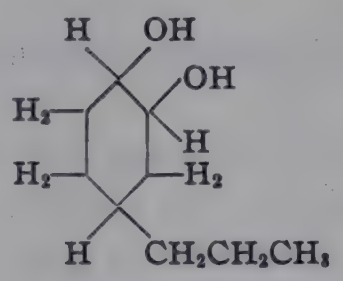
[99] E. Hägglund, *Holzchemie*, p. 200; see ref. 76, p. 457.

4. Oxidation and Hydrogenation

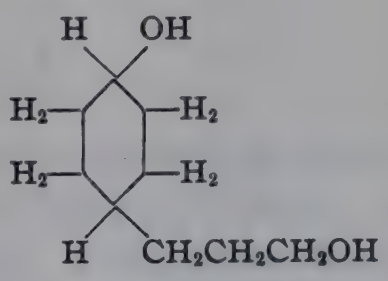
The production, by drastic oxidation, of smaller structural fragments of value in establishing the structure of lignin has not been successful, because on oxidation only oxalic acid, formic acid, and carbon dioxide are obtained. On oxidation of spruce lignin with chromic acid, 6% acetic acid is found,[23] which corresponds to about one CH_3—C— group per lignin building unit of a molecular weight of 840. Reduction with hydriodic acid and phosphorus gives a mixture of hydrocarbons from which no definite compound can be separated.[29] The catalytic hydrogenation of lignin has been more successful; from such experiments very significant results regarding the structure of the lignin building stone have been obtained.[100, 101, 102] When methanol lignin from maplewood is subjected to the action of hydrogen at 250 atm. and 250–260°C. in the presence of copper chromite or Raney nickel as catalyst, the following products are obtained: 11% 4-*n*-propyl-1-cyclohexanol, 3.2% 4-*n*-propyl-1,2-cyclohexanediol, and 24% 4-(ω-hydroxy-*n*-propyl)-1-cyclohexanol,



4-*n*-Propyl-1-cyclohexanol



4-*n*-Propyl-1,2-cyclohexanediol



4-(ω-Hydroxy-*n*-propyl)-1-cyclohexanol

in addition to methanol which originates from the methoxyl groups, some water, and a colorless resin of the general composition $(C_6H_{11}O)_x$. These results indicate that a large proportion of the lignin is composed of building stones having the phenylpropane skeleton. Unfortunately, these results do not permit conclusions to be drawn as to the mode of linkage of the individual building stones.

5. Methylation

The alkylation of lignin has often served for the characterization of lignin and its derivatives.[103] Methylation of hydrochloric acid spruce

[100] E. E. Harris, J. d'Ianni, and H. Adkins, *J. Am. Chem. Soc.*, **60**, 1467 (1938).
[101] H. Adkins, R. L. Frank, and E. S. Bloom, *J. Am. Chem. Soc.*, **63**, 549 (1941).
[102] H. Hibbert and coworkers, *J. Am. Chem. Soc.*, **63**, 3052, 3056, 3061 (1941).
[103] E. Heuser, R. Schmidt, and L. Gunkel, *Cellulosechem.*, **2**, 81 (1921).

lignin with diazomethane in ether suspension increases the methoxyl content from 15.5 to 19.8%,[104] whereas in anhydrous cyclohexanol suspension the methoxyl content is increased to 21.5%.[105] Isolated spruce native lignin, when methylated in ether suspension, gives a partly methylated spruce lignin with a methoxyl content of 18.3% which, on further methylation with diazomethane in dioxane solution, is increased to 21.5%.[12] Methylation of hydrochloric acid spruce lignin with dimethyl sulfate and sodium hydroxide gives a methylated lignin with a final methoxyl content of 32.4%.[105] The same methoxyl content is obtained when diazomethane-methylated spruce native lignin is further methylated with dimethyl sulfate.[7, 12] Methylation of lignosulfonic acid from spruce with diazomethane leads to a partially methylated product having a methoxyl content of 19.2%[64] which, on further methylation with dimethyl sulfate, gives a completely methylated lignosulfonic acid with a methoxyl content of 27.7%,[28, 64] indicating that the number of hydroxyl groups in the lignin molecule has not been altered by the sulfonation.[77]

6. Substitution Reactions

Chlorination of lignin leads to the formation of undefined products because oxidation and substitution in the positions on the ring next to the methoxyl group occur with simultaneous removal of methoxyl groups. Bromination under carefully controlled conditions results in the introduction of one bromine atom, which corresponds to the substitution of one hydrogen atom per lignin building stone.[91] On nitration of methylated lignin with nitrogen dioxide, substitution also occurs with the introduction of one nitro group per lignin building stone.[106] Since the brominated lignin can be nitrated and vice versa, two hydrogen atoms capable of being substituted are present in each lignin building stone. The reactivity of one hydrogen atom in the benzene ring of each lignin building stone is also shown by the action of mercuric acetate with methylated lignin[91, 107] or methylated glycol lignin,[108] whereby one acetoxymercuric group per lignin building stone is introduced.

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[104] K. Freudenberg and H. Hess, *Ann.*, **448**, 133 (1926).

[105] F. E. Brauns and H. Hibbert, *Can. J. Research*, **13B**, 78 (1935).

[106] K. Freudenberg and W. Dürr, *Ber.*, **63B**, 2713 (1930).

[107] K. Freudenberg and H. F. Müller, *Ber.*, **71B**, 2500 (1938).

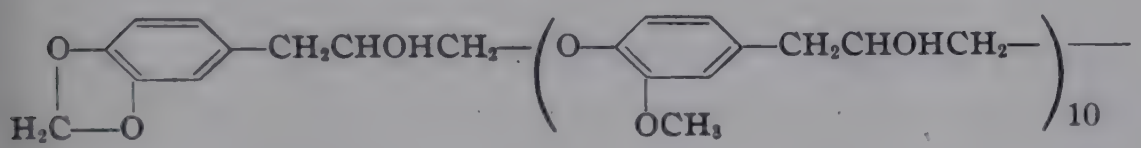
[108] K. R. Gray, F. E. Brauns, and H. Hibbert, *Can. J. Research*, **13B**, 48 (1935).

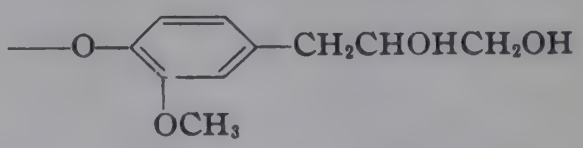
7. Nature of Combination of Lignin Building Stones

In spite of over a hundred years of lignin chemistry, the structure of lignin is still unsolved. Considerable progress, however, has been made during the last fifteen years.

Although many constitutional schemes have been presented for lignin, [109–114] only the ones which appear to be most significant at the present time will be discussed. As early as 1897, Klason[73] recognized the close relationship existing between lignin and coniferin (the glucoside of coniferyl alcohol), which is present in the cambial sap of spruce. He concluded that lignin is a condensation or polymerization product of coniferyl or oxyconiferyl alcohol, since he found that such products show properties similar to those of lignin. Later[71] he suggested that coniferyl aldehyde may be the basic building stone of lignin.

On the basis of his experimental results, Freudenberg[18, 84] in 1929 assumed that lignin is a condensation polymer of simple building stones consisting of an aromatic nucleus having a three-carbon side chain. He formulated "primary lignin" as a linear polymer chain.





In spite of the fact that this scheme explains some of the lignin reactions, it is not in harmony with others, such as the transformation into "secondary lignin" and the behavior of lignin toward hydriodic acid.

A study of the condensation of coniferyl alcohol revealed that the alcoholic hydroxyl group is eliminated with a hydrogen of the nucleus of a second molecule.

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[109] C. F. Cross, E. J. Bevan, and C. Beadle, *Ber.*, **26,** 2520 (1893).

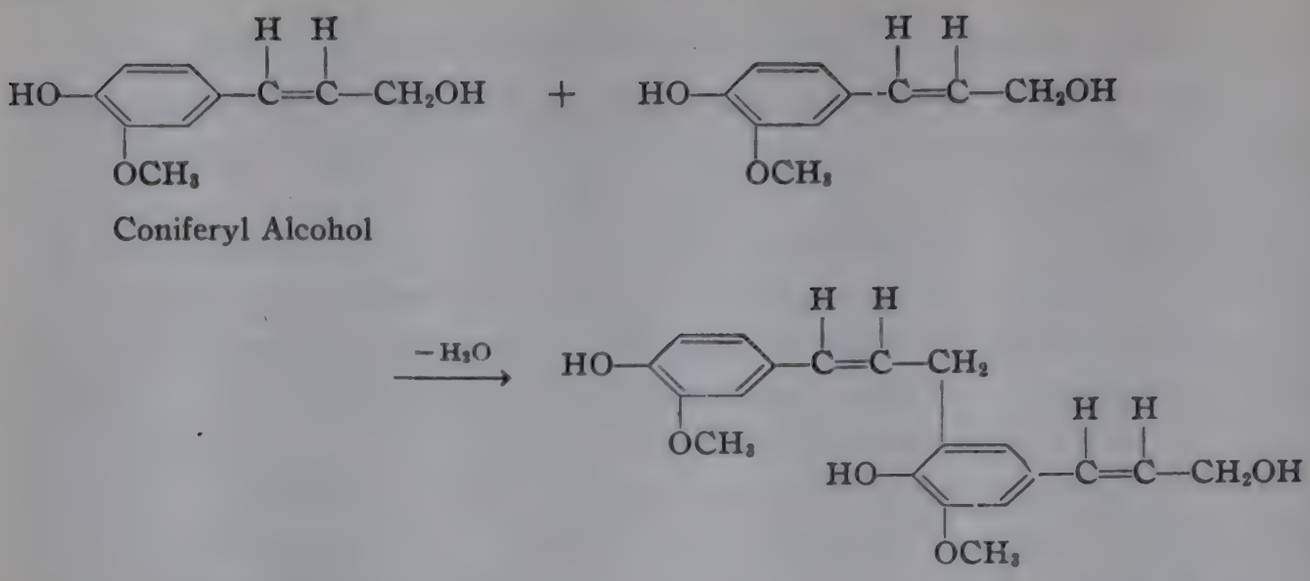
[110] A. G. Green, *Z. Farben- u. Textilchem.*, **3,** 97 (1904).

[111] K. Kürschner, *Zur Chemie der Ligninkörper.* F. Enke, Stuttgart, 1925, p. 37.

[112] T. Pavolini, *Industria chimica*, **6,** 1367 (1931).

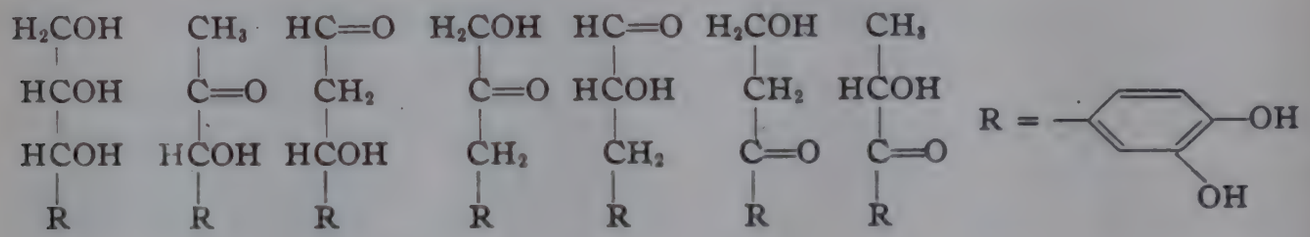
[113] W. Schrauth, *Z. angew. Chem.*, **36,** 149 (1923).

[114] W. Fuchs, *Z. angew. Chem.*, **44,** 111 (1931).



Coniferyl Alcohol

Taking into consideration such a condensation reaction and the amount of oxygen present in lignin, Freudenberg concluded that the building stone of lignin must be a phenolpropane derivative in which the stage of oxidation of the side chain is the same as that in glycerol.[115, 116] The following seven such derivatives[117] are possible (R is a pyrocatechol group):



According to Freudenberg, any one of these derivatives, for example, guaiacylglycerol (a more descriptive name would be 1-(4-hydroxy-3-methoxyphenyl)-1,2,3-propanetriol) (X) or acetylguaiacylcarbinol (more descriptive names would be acetyl(4-hydroxy-3-methoxyphenyl)carbinol or 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone) (XI), may unite with any other in such a way that ether linkages are formed (XII and XIII). Several of such building stones can react with each other thus forming larger units (XIV and XV). He further assumed that the primary hydroxyl group of the side chain is then split off by nuclear condensation similar to that of the coniferyl alcohol condensation with formation of chroman rings (XVI) or furan rings (XVII).

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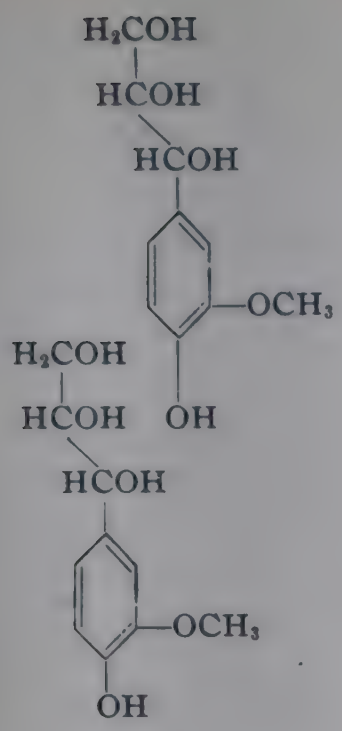
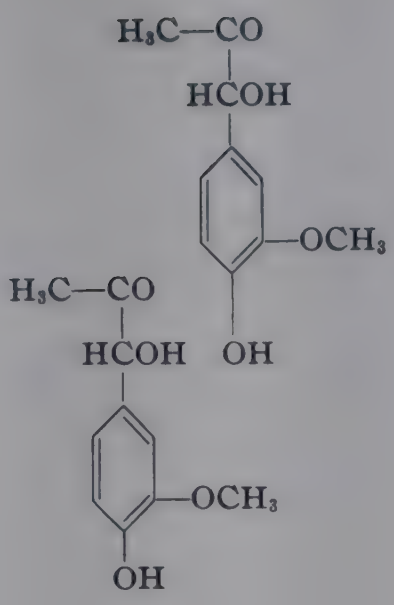
[115] K. Freudenberg, *Tannin, Cellulose, Lignin*, p. 135; see ref. 49, p. 455.

[116] K. Freudenberg and W. Lautsch, *Naturwissenschaften*, **27**, 227 (1939).

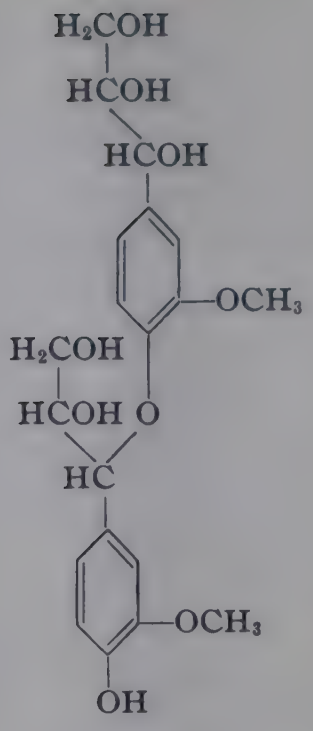
[117] H. Hibbert, *J. Am. Chem. Soc.*, **61**, 725 (1939).



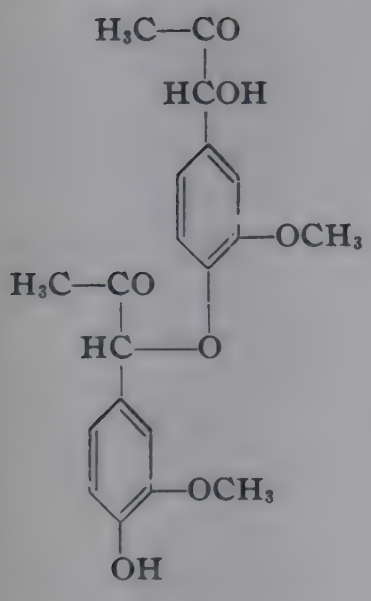
X



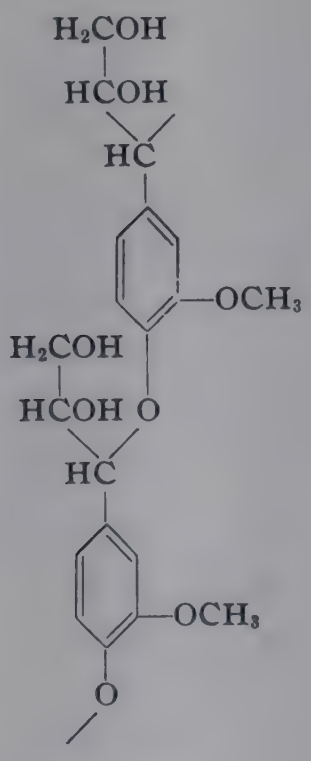
XI



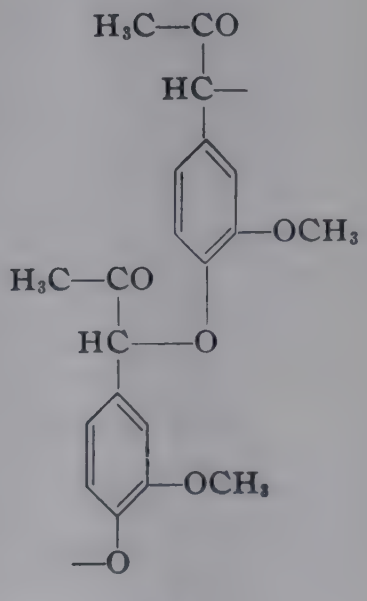
XII



XIII



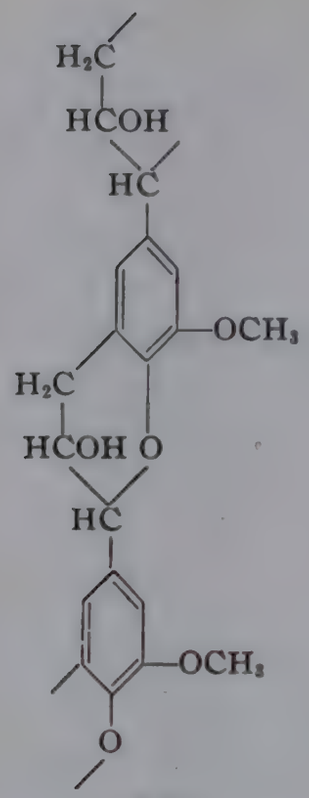
XIV



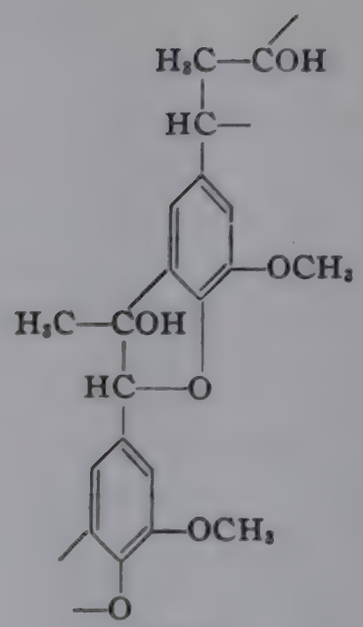
XV

(Formulas XVI and XVII continued on next page)

Depending upon the substituents of the phenolic hydroxyl groups, vanillyl, isovanillyl, or piperonyl groups may be formed. In hardwood lignins with their higher methoxyl contents, between one-third and one-half of



XVI



XVII

the R groups are syringyl groups. The formation of 25% vanillin from lignin indicates that at least one-fourth of the lignin molecule consists of the vanillin group.[118]

The finding by Hibbert and coworkers[119, 120, 121] of small quantities of acetovanillone and guaiacol in addition to vanillin on treatment of sulfite waste liquor from sprucewood with sodium hydroxide under pressure, and of pyrogallol 1,3-dimethyl ether, syringaldehyde, and acetosyringone from lignosulfonic acid from maplewood under the same conditions, indicates the presence of aromatic groups with side chains of at least 2 C atoms.

Derivatives of phenylpropane have also been isolated by Hibbert[122, 123, 124] from the aqueous solutions of the alcoholysis products of wood. In the preparation of glycol lignin and other alcohol lignins from

[118] K. Freudenberg in *Annual Review of Biochemistry*. Vol. 8, Annual Reviews, Inc., Calif., 1939, p. 81.

[119] F. Leger and H. Hibbert, *Can. J. Research*, **16B**, 68, 151 (1938); *J. Am. Chem. Soc.*, **60**, 565 (1938).

[120] I. K. Buckland, G. H. Tomlinson, and H. Hibbert, *J. Am. Chem. Soc.*, **59**, 597 (1937).

[121] A. Bell, W. L. Hawkins, G. F. Wright, and H. Hibbert, *J. Am. Chem. Soc.*, **59**, 598 (1937).

[122] A. S. MacInnes, E. West, J. L. McCarthy, and H. Hibbert, *J. Am. Chem. Soc.*, **62**, 2803 (1940).

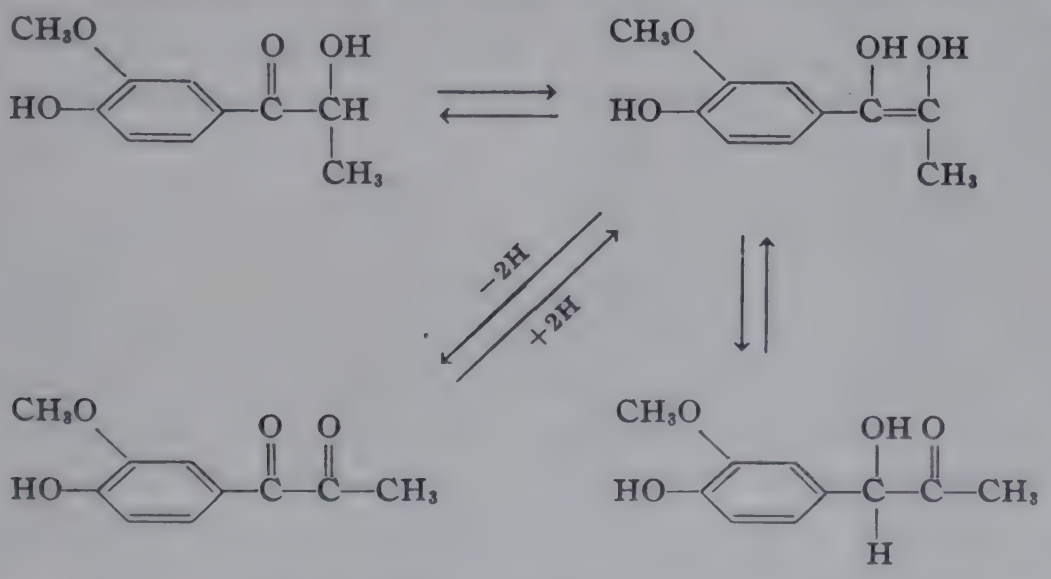
[123] H. Hibbert and coworkers, *J. Am. Chem. Soc.*, **60**, 2815 (1938); **61**, 509, 516 (1939).

[124] J. J. Pyle, L. Brickman, and H. Hibbert, *J. Am. Chem. Soc.*, **61**, 2198 (1939).

sprucewood, a considerable portion of the dissolved lignin remains in the aqueous mother liquor of the alcohol lignin as "soluble lignin."[45] An investigation of this soluble lignin from the ethanolysis of maplewood reveals the presence of syringaldehyde, vanilloyl methyl ketone, syringoyl methyl ketone, α-ethoxypropiovanillone, and α-ethoxypropiosyringone. As alcoholysis is the only reaction which takes place in this process and ethoxyl groups are not present in lignin, syringaldehyde, vanilloyl methyl ketone, and syringoyl methyl ketone may be true scission products of lignin, whereas α-ethoxypropiovanillone and α-ethoxypropiosyringone must have been formed by ethylation of the corresponding hydroxy compounds. All of these compounds are related to the various types proposed by Freudenberg and to 4-hydroxy-3-methoxy-1-*n*-propylbenzene obtained on distillation of lignin from corncobs with zinc dust.[125]

The isolation of these products supports experimentally Freudenberg's view regarding the structure of the lignin building stone. Since these phenylpropane derivatives are soluble in water, and since native lignin is insoluble, it is evident that these products do not represent native lignin but are simple degradation products. Native lignin must be a condensation or polymerization product of these building stones.

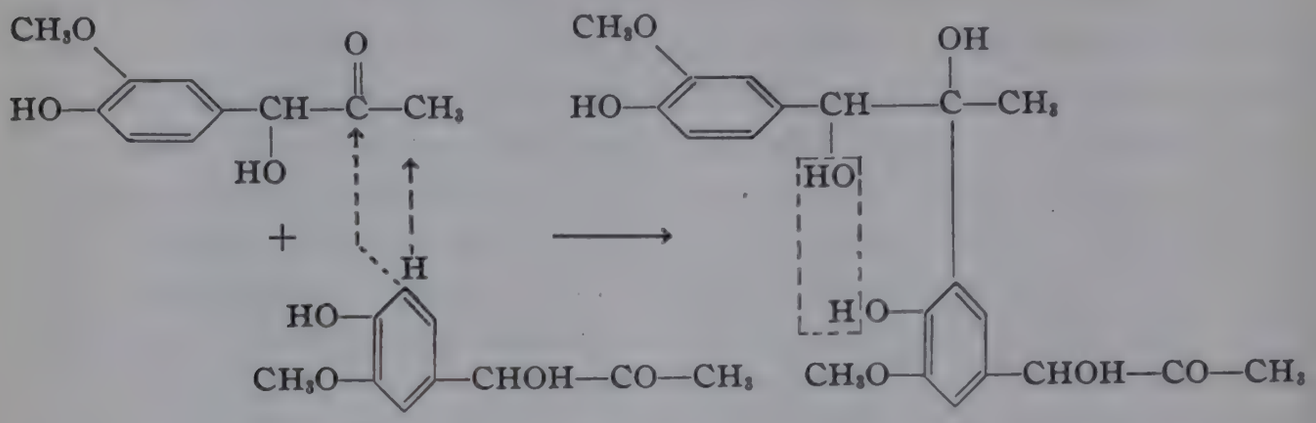
Hibbert[118] arrives at the following conclusions regarding the polymerization: α-hydroxypropiovanillone and α-hydroxypropiosyringone are very sensitive compounds and, under the influence of mild reagents, undergo intramolecular dismutation transformations involving hydrogen migrations and oxidation-reduction systems, the intermediate product being an ene-diol.



These derivatives with a phenolic group and a carbonyl group or an unsaturated ethylene linkage have a strong tendency to undergo ortho-

[125] M. Phillips, *J. Assoc. Official Agr. Chem.*, **15**, 118 (1932).

and para-nuclear condensations with formation of condensation polymers. An example of this type of condensation is shown below.



In this reaction a furan ring is formed similar to that proposed by Freudenberg. Their mechanisms differ only in the order in which the various changes are assumed to occur. With the syringyl group present, both positions ortho to the phenol groups are blocked and another mechanism must be postulated.

The foregoing discussion regarding the properties of lignin may be summed up briefly as follows. No clear-cut picture may be presented at this time which represents the molecular structure of the simple lignin building units. Evidence has been developed, however, which indicates that, in its simplest form, lignin may in large part be built up of phenylpropane building stones with phenolic hydroxyls or methoxyls in the 3,4- positions. The propyl radical likewise at times appears to contain an enolizable carbonyl, which, from the standpoint of the pulp technologist, is the most significant part of the structure, since fixing of the enolic character by methylating with diazomethane hinders or even stops completely the reactions of technical delignifications.

This phenylpropane structure is supported by the production of 4-hydroxy-3-methoxy-*n*-propylbenzene from the zinc dust distillation of corncob lignin[125]; by the hydrogenation of lignin to 4-*n*-propyl-1-cyclohexanol and its related propanol derivative, 4-(ω-hydroxypropyl)cyclohexanol, and other similar compounds; and by the formation of α-ethoxypropiovanillone and related compounds as the result of the ethanolysis of lignin. The 1,3,4-substituted aromatic ring is also indicated by the formation of compounds like veratric acid on oxidation of methylated lignin and of protocatechuic acid from the alkaline fusion of lignin.

Any satisfactory structure not only will need to show the origin of the breakdown products of lignin described above, but it will also have to agree with the quantitative picture which has resulted from the studies of

the methylation of spruce native lignin, unless they are shown to be in error. Thus, if the formula is to represent the structure of alcohol-soluble spruce native lignin, it will need to show the presence of one phenolic hydroxyl and one enolic hydroxyl per molecular weight of approximately 840 (relating in some way to the combination of five of the above substituted phenylpropane radicals). It will need to show, in addition, a total of four methoxyls and a total of four hydroxyls for the same structure, for the accuracy and reproducibility achieved in the study of native lignin is such as to suggest that the analytical results are really significant.

Finally, the structure will have to harmonize with the ultraviolet absorption spectrum of lignin, which has been substantiated too many times to lead to any question of its general character, because native lignin, isolated lignin, and many lignin derivatives may be identified by this means.

D. NATURE OF THE OTHER NONCARBOHYDRATE COMPOUNDS IN WOOD AND STRAW

The other noncarbohydrate compounds in wood and straw are present in minor amounts. In wood they consist of resins, tannins, dyestuffs, fats, waxes, proteins, and mineral components. The amounts vary widely with the species of the wood.

The resins consist of the resin acids, the resin alcohols, and the resenes, the last being insoluble in alkali. The resins, which vary in coniferous woods from 2.3 to 25% and in deciduous woods from 0.7 to 3%, are the basis for the large naval stores industry. They can be extracted together with the fats and waxes by means of organic solvents. They are changed with the seasoning of the wood; thus, the trouble they cause in the pulp and paper industry is reduced. In the sulfite process they remain partly in the pulp, while in the soda and kraft processes they are found in the tall oil.

The tannin content of wood varies widely with the species and is found chiefly in the bark, although some is also present in the wood itself. For instance, the barks of western larch, western yellow pine, and hemlock contain 10.6 to 10.9%, whereas the woods contain 6.7%, 8.9%, and 1%, respectively.[126] The tannins may be classified in two groups: the depsides or polyesters, which are hydrolyzable; and the catechol tannins or phlobatannins, containing carbon-carbon links between the units, which cannot be hydrolyzed. They are soluble in water and decompose when heated with aqueous mineral acids. The phlobatannins when treated in this way give red precipitates known as phlobaphenes. Insofar as the tannins are not

[126] H. K. Benson and F. M. Jones, *Ind. Eng. Chem.*, **9**, 1096 (1917).

changed during the pulping process, they are removed with the waste liquor. In this connection, a structural relationship between the catechol tannins and lignin has been suggested.[117, 127]

The dyestuff content of woods usually used for pulping is very low. These natural plant pigments are, in general, phenolic compounds such as flavones and anthocyanins. They are usually glucosides, and, therefore, bear a strong structural resemblance to the catechins and, indeed, lignin.[117] As natural dyestuffs are mostly soluble in alkali, they are removed in the alkaline pulping process. In the sulfite process, however, they remain in the pulp and may affect its color.

The proteins and the mineral components in woods amount to 1.3% and 0.4 to 1.1%, respectively, and have no effect on the pulping process. The high content of silica prevents straws from being used in the sulfite process. The minerals are difficult to remove from the cellulose and have a deleterious effect on some of the properties of cellulose derivatives.

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[127] H. Erdtman, *Svensk Papperstidn.*, **42**, 115 (1939).

Chapter VI

PREPARATION OF CELLULOSE FROM ITS NATURAL SOURCES

A. WOOD PULP

CHARLES M. KOON

The isolation of cellulose from wood by any of the three most important commercial processes (sulfite, sulfate, and soda processes) employed today depends for its success upon the proper application of basic knowledge pertaining to at least three fields of science; namely, wood technology, chemistry, and physics.

Wood technology is important, for it is from this field that we derive our knowledge that wood is not a homogeneous substance, but rather a somewhat systematic arrangement of interconnected cells, each of which is heterogeneous both physically and chemically. These cells the pulp technician calls fibers; and from these cells the term "cellulose" is derived. The structural characteristics of fibers and the manner in which they are arranged and bound together in wood have an important bearing on the penetration of cooking liquors, the course of pulping reactions, and the physical, chemical, and colloidal properties of the "cellulose" (pulp) itself.

The primary chemical reactions between pulping agents and the isolated components of wood are somewhat better known today than they were fifteen, ten, or even five years ago. With this increasing knowledge, however, has come the realization that, in addition, the secondary reactions among the primary products, and between the primary products and the residual original components, must be more thoroughly investigated.

Successful applications of physics and physical chemistry aid in a better understanding of such processes as the capillary penetration of chips, the distribution of heat within the digester charge, the solution and recovery of gaseous pulping agents, and a thousand and one other factors which affect particularly the economy of the pulp mill.

1. Objectives of Chemical Pulping

The objectives of chemical pulping may be stated very simply. They are: (1) to separate the individual fibers from each other with a minimum of mechanical damage, and (2) to purify the fibers chemically to such a degree that they will perform satisfactorily in subsequent manufacturing operations. The first objective is accomplished by weakening the material

between the fibers to such an extent that, upon subsequent disintegration, the rupture occurs within this region rather than within the fiber itself; the second, by selecting a reagent which is reasonably specific toward lignin, and by so controlling the process that this reagent is directed to the areas within the chip where the lignin is most concentrated.

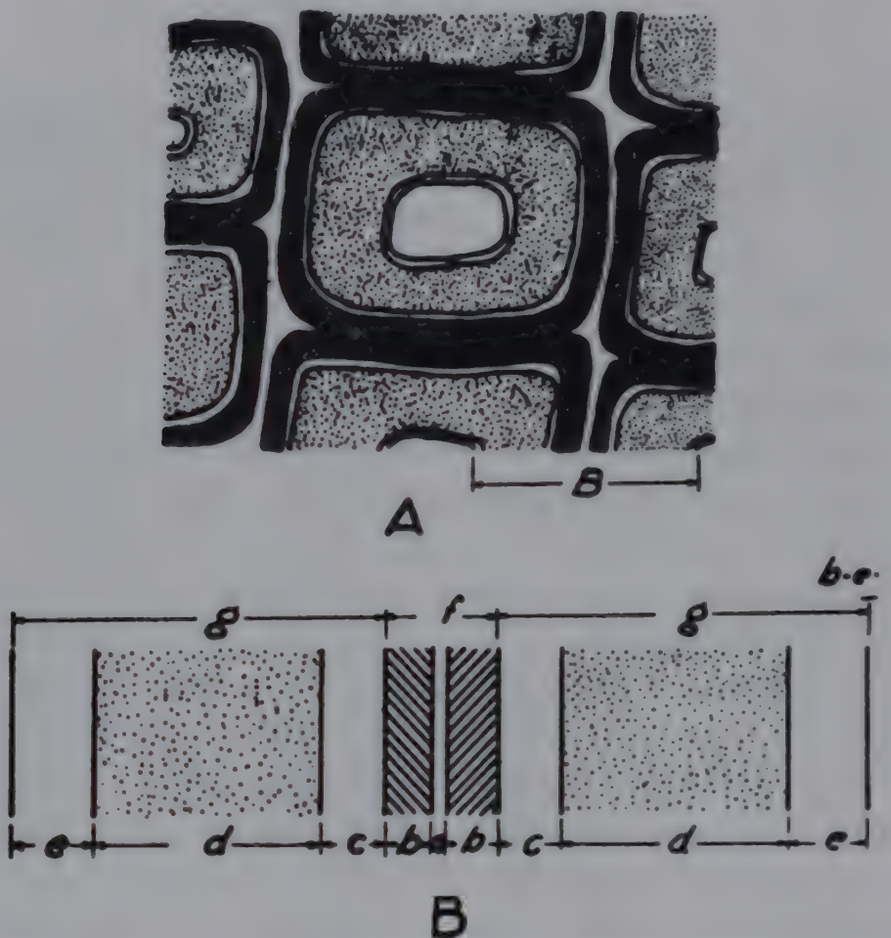

FIG. 1.—THE COMPOUND CELL WALL OF WOOD FIBERS (JAHN AND HOLMBERG[2]).
Cell-wall parts according to I. W. Bailey.

A.	Cross section of a fiber.	*d*.	Central layer secondary wall.
B.	Section of two adjacent cell walls.	*e*.	Inner layer secondary wall.
a	Intercellular substance.	*f*.	Compound middle lamella.
b.	Primary (cambial) wall.	*g*.	Complete secondary wall.
c.	Outer layer secondary wall.	*b-e*.	Complete cell wall of one fiber.

Some familiarity with the microstructure of wood is essential to an understanding of the obstacles which oppose the complete attainment of the objectives stated above. Space has already been devoted to one important aspect of this in Section B of Chapter III. Figure 1 shows the wood technologist's conception[1, 2] of a typical compound cell wall as seen in a sec-

[1] I. W. Bailey, *Ind. Eng. Chem.*, **30**, 40 (1938).

[2] E. C. Jahn and C. V. Holmberg, *Paper Trade J.*, **109**, 30 (Sept. 28, 1939).

tion cut parallel with the grain of the wood. Figure 2 is a schematic view, somewhat less enlarged, showing the orientation and position of the various wood elements relative to each other.[3] This shows the occurrence of bordered pits on the radial walls of each tracheid. During the life of the tree these are a means for the transfer of solutes from one cell to another,

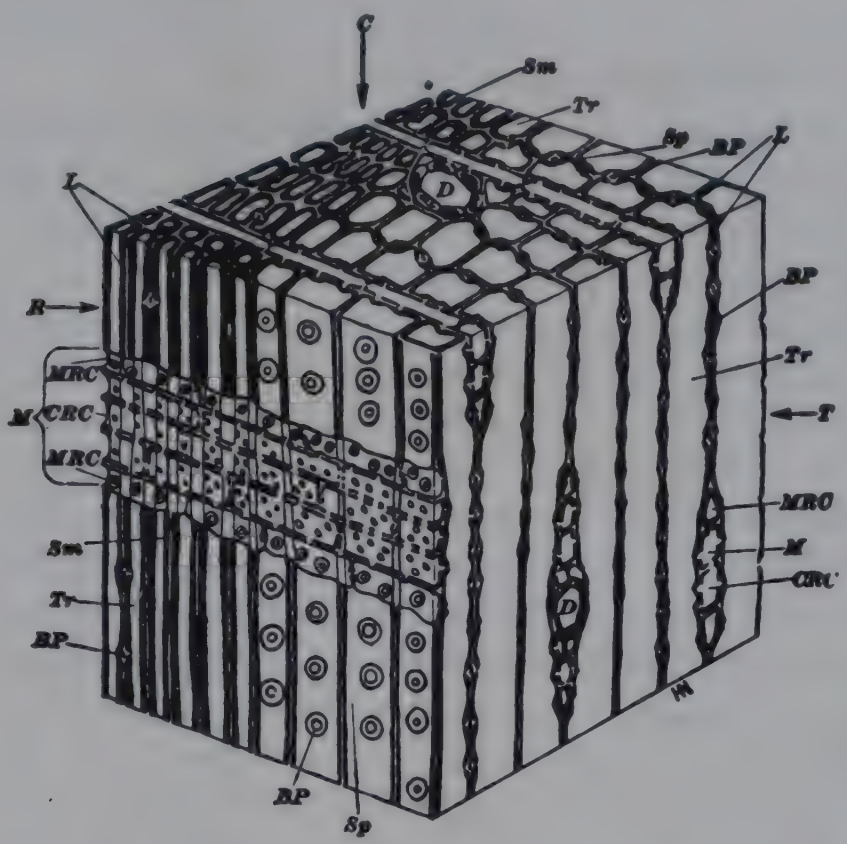

FIG. 2.—DIAGRAM OF A SMALL BLOCK OF SPRUCEWOOD, GREATLY ENLARGED, SHOWING A PART OF ONE ANNUAL RING (LEE[3]).

C.	Cross section.	*Tr.*	Tracheid.
R.	Radial section.	*BP.*	Bordered pit.
T.	Tangential section.	*L.*	Middle lamella.
D.	Resin duct.	*M.*	Medullary ray.
Sm.	Summerwood.	*CRC.*	Central ray cell.
Sp.	Springwood.	*MRC.*	Marginal ray cell.

and are generally believed to perform a similar function during the pulping operation. The significance of the morphological features illustrated by these drawings will now be discussed in some detail.

For some time, it has been thought that a large portion of the lignin in wood is concentrated in the compound middle lamella (the region represented in Figure 1 by the portion labelled "intercellular substance") plus

[3] H. N. Lee in *The Manufacture of Pulp and Paper.* 3rd ed., Vol. III, Sec. 1, McGraw-Hill, New York, 1937, p. 13.

the adjacent primary wall on either side. More recently, this belief has been supported by the work of A. J. Bailey,[4] who devised a microtechnique for isolating enough of the middle lamella to permit its chemical analysis. Bailey reported the following composition for the middle lamella of the Douglas fir: lignin 71%, cellulose 4%, pentosans 14%. It is probable that most of the cellulose reported was actually in the primary wall, which would leave the intercellular substance practically all lignin, with very small amounts of hemicellulose.

This does not mean, however, that all the lignin is found in the middle lamella. The best evidence at present indicates that the cellulose lattice of the secondary wall is interspersed and perhaps combined with a hemicellulose lattice which, in turn, is associated in some manner with lignin (always a fairly small percentage). In order to reach the middle lamella, the cooking liquor, which through penetration has filled the lumen or central cavity of each fiber, must either diffuse through this complex lattice or find some means of circumventing it. In this respect, the bordered pits may play a dual role, for they not only assist in the migration of liquor from one fiber to the next but, at the same time, also bring the liquor into almost direct contact with the middle lamella, its ultimate destination. Upon solution of the middle lamella, the reverse of this liquor penetration process begins. That is, the dissolved reaction products must diffuse out of the chip and into the main body of the cooking liquor. It should be made clear that *maceration does not occur during the cook;* the physical stresses involved in blowing, washing, and screening are required to effect complete liberation of the individual fibers from each other.

Lewis and Richardson[5] prepared a series of raw alkaline pulps from the same original raw material; these pulps contained progressively smaller amounts of lignin. The beating characteristics of these pulps and their swelling behavior in cuprammonium hydroxide were determined. As the lignin content decreased from 22.2 to 8.6%, the pulps beat more readily, and the maximum strength attained by the corresponding handsheets became greater. At the lowest lignin content value, the pulp strength characteristics approached those of a raw kraft pulp, as might be expected; at higher lignin values, the pulps were of inferior strength. In the case of the pulp containing 22.2% of lignin, application of cuprammonium solution had practically no effect. As the lignin content decreased, a phenomenon called "ballooning" began to occur upon contact between the fiber and the

[4] A. J. Bailey, *Paper Ind.*, **18**, 379 (1936); *Ind. Eng. Chem., Anal. Ed.*, **8**, 52, 389 (1936).

[5] H. F. Lewis and C. A. Richardson II, *Paper Trade J.*, **109**, 48 (Oct. 5, 1939).

reagent. It appeared that the swelling of the cellulose was restricted by a more resistant sheath which surrounded the fiber; wherever this sheath was absent or attenuated, the fiber would swell to several times its original diameter, giving somewhat the appearance of a string of fat sausages. The susceptibility of the fiber to this ballooning action seemed to be a direct function of the degree of its delignification. These investigators, therefore, supported the hypothesis that wood fibers, as they naturally occur, are surrounded by a sheath relatively high in lignin content; they also postulated that until this sheath is removed, the fibers cannot properly be beaten and formed into a sheet.

With this background established, the objectives of chemical pulping in more specific terms can now be restated tentatively as follows: (1) to weaken or destroy the intercellular substance; (2) on the assumption that the sheath of Lewis and Richardson was identical with the primary wall of Figure 1, to remove this primary wall to such an extent that the fiber will lend itself readily to subsequent manufacturing operations; (3) to remove substantial proportions of the lignin found in the secondary wall, if the pulp is to be used in conversion processes where high brightness or high purity is required. The last-named objective is deliberately stated to imply that not all the lignin should be removed from the secondary wall by the cooking operation. In the first place, it has not yet been proved that lignin must be removed in order to attain a pulp of satisfactory color; and in the second place, it is the function of bleaching and special purification processes to remove the last traces of lignin and hemicelluloses when the pulp is to be used for cellulose derivatives. (See Chapter VII.)

2. Pulping Agents

So far, it has been shown that several mechanical obstacles oppose the successful execution of the pulping process. These would be less formidable if the carbohydrate components of the wood were inert under the conditions which exist during the cook or if an economical reagent could be found which would be more specific toward lignin. None of the pulping agents in commercial use today are absolutely specific in their effect. Some are more specific than others, however, and the following list is an attempt to classify them on this basis:

Most specific:	Chlorine
	Sodium sulfide plus sodium hydroxide
	Sulfurous acid plus a bisulfite
Least specific:	Sodium hydroxide

Even the best of these four agents, when used under ideal conditions, probably has a slight effect upon the hemicelluloses; and, under commercial conditions, the cellulose itself is degraded to an appreciable degree. Chlorine is included in the above list for scientific reasons. Wood in the form of shavings can be pulped very well by alternate treatments with chlorine and monoethanolamine.[6] However, chlorine is not used in the commercial pulping of wood, except in the sense that the chlorination of pulp can perhaps be considered a continuation of the pulping process.

3. The Importance of Uniformity in Pulping

In spite of the number and variety of facts embraced by the field of pulp technology, there is one concept which may well serve as a common denominator for most of them. This is the concept of uniformity. It pertains to the daily production of a six-hundred-ton pulp mill as well as to the treatment of the individual fiber; it applies to the conditions of a twenty-five-ton sulfite digester as well as to the reactions within the individual chip. We have already pointed out that wood is a heterogeneous substance, that the middle lamella is protected by several layers of carbohydrate material, and that there is a dearth of commercial agents which are specific in their action on lignin. Nevertheless, there is a degree of pulping action which is optimum for the particular product in which the pulp will ultimately be used. The closer this degree of pulping can be approached by every fiber, the more successful the process will have been from the technical, and often from the practical, point of view.

(*a*) *Raw Material*

The importance of using a uniform raw material becomes obvious. If spruce is considered an ideal species for pulping, one of the reasons is the lack of marked differentiation between its springwood and summerwood. Once a pulping schedule has been adopted by a pulp mill for a certain raw material, it is expedient to keep the quality of this raw material as constant as possible, even though such wood yard control may be an expensive and time-consuming process. Morgan and Dixson[7] have found that chip length is an important variable to be controlled, since short chips may be

[6] H. H. Houtz and E. F. Kurth, *Tech. Assoc. Papers*, Ser. 22, 329 (1939); *Paper Trade J.*, 109, 38 (Dec. 14, 1939); G. J. Hajny and G. J. Ritter, *Paper Trade J.*, 111, 131 (Nov. 28, 1940).

[7] H. Morgan and H. P. Dixson, Jr., *Tech. Assoc. Papers*, Ser. 21, 364 (1938); *Paper Trade J.*, 107, 38 (Aug. 18, 1938).

overcooked before longer ones have been pulped to a sufficient degree. A chip length of 0.75 inch will give satisfactory results in general.

(*b*) *Heat Distribution in the Digester*

The introduction of liquor circulating and heating systems has made possible a marked improvement in the control and uniformity of pulping degree. When the introduction of steam at the bottom and the relief of gases at the top were the only means of distributing the heat and cooking liquor throughout the digester charge, a temperature differential of 25°C. between respective zones of the digester was not an uncommon condition. Since the reaction rate in either sulfite[8] or alkaline[9] pulping doubles with a ten-degree temperature rise, it is obvious that a uniform product could not be secured under such circumstances.

(*c*) *Temperature Schedule and Liquor Penetration*

The same reasoning applies to the selection of the temperature schedule. Until the chips have been uniformly penetrated by the liquor, the temperature must not be raised to the point where reaction proceeds at an appreciable rate. The rate of penetration depends primarily upon the nature and condition of the raw material, particularly upon its moisture content, but it can be increased by such expedients as increasing the pressure,[7, 10] or increasing the temperature. McGovern and Chidester have demonstrated that wetting agents as a class do *not* facilitate penetration of chips by cooking liquor.[11] It seems that, although wetting of the chip surface by the liquor may be essential, the rate of this action is not the limiting factor; the capillary flow through the lumen is believed to be more important. Since wetting agents decrease the surface tension of water, it might be expected that their presence would *retard* capillary flow. In any event, McGovern and Chidester actually observed a decrease in penetration rate when certain wetting agents were added to the system.

(*d*) *Rate of Pulping as a Function of Chemical Concentration*

At each point in the cook, the rate of pulping is a direct function of the concentration of the active agent. Initially, this concentration can be in-

[8] R. N. Miller, W. H. Swanson, *et al.*, *Chemistry of the Sulfite Process*. Lockwood Trade J. Co., New York, 1928, p. 77.

[9] W. J. Nolan and D. W. McCready, *Paper Trade J.*, **102,** 36 (Jan. 23, 1936); *Tech. Assoc. Papers*, Ser. **19,** 237 (1936).

[10] E. B. Brookbank, Jr., *Paper Trade J.*, **108,** 30 (Feb. 16, 1939).

[11] J. N. McGovern and G. H. Chidester, *Paper Trade J.*, **111,** 35 (Dec. 12, 1940).

creased by either using more chemical or adding less water. From the standpoint of chemical recovery, it is desirable to use as little water as possible, since eventually this water has to be removed by the multiple-effect evaporators. However, the resistance of pulp to degradation by the high chemical concentrations is less than one might suppose, even in the presence of appreciable amounts of lignin. Doubtless the fact that the liquor really comes in contact with the carbohydrate layers first, as explained above, is partially responsible. For optimum results, therefore, the chemical concentration should be kept at a moderate value at all times, although, of course, there is a limit to the sacrifices which can be made in production and operating economy.

Various investigators have proposed schemes by which this control of concentration can be effected. One of these is to inject strong liquor during the cook at such a rate that the concentration range is optimum throughout.[12] Another is to schedule a number of digesters in such a manner that liquor can be pumped from one to the other in a countercurrent fashion. The strongest liquor comes in contact with the pulp at a moderate temperature just before the charge is blown. Leaving this digester, the liquor is injected at a somewhat higher temperature into the next rawer charge, and so forth. In this manner, theoretically, extremes in concentration are avoided without sacrificing production or operating economy.[13] A third scheme, which has received little attention in the literature, perhaps because it is so obvious, is to increase the amounts of both chemical and water, but in such a ratio that the depletion of chemical by the reaction does not reduce the concentration below the value which is essential to a reasonable reaction rate. The fact that none of these schemes are used today on a commercial scale, at least in this country, might be cited as evidence that they are inherently impractical. However, when high-quality pulps cannot be obtained from abroad, as sometimes happens, it is conceivable that the definition of practicality may be altered.

(*e*) *Selection of Pulping Agents*

A further device which is used, perhaps unconsciously, for promoting uniformity is the selection of those pulping agents which are most specific in lignin removal. The economic advantage of sodium sulfate over sodium carbonate is not the only reason why practically all the new pulp mills have been built for the application of the kraft process. Kraft liquor is

[12] C. R. Mitchell and J. H. Ross, *Quart. Rev. Forest Products Laboratory of Canada*, No. 5, Part 1, 103 (1931).

[13] G. A. Kienitz, *Holz Roh- u. Werkstoff*, **1**, 30 (1937).

definitely superior to soda liquor for coniferous species in that it removes lignin with less damage to the cellulose and with less removal of hemicellulose. The kraft process has a similar advantage over the sulfite process in that it preserves fiber strength to a greater extent. Furthermore, the Scandinavian mills have found it expedient to carry the kraft digestion only to a certain point, corresponding to a fairly high lignin content, and to employ chlorine, an even more specific agent, for continuing the delignification. It has been remarked above that wood shavings can be pulped very effectively by a chlorination process. However, the reaction products of chlorination are not entirely soluble either in water or in the chlorine solution. Accordingly, alternate treatments with chlorine and with a slightly basic compound, such as pyridine or monoethanolamine, are required. So far, the pulping of chips by such a process has not been successful and, even if it were, the amounts of chlorine required for lignin removal plus the relative cost of chlorine as compared with salt cake, soda ash, sulfur, or lime would tend to discourage commercial exploitation. Ritter,[14] it is true, has obtained some interesting results from the chlorination of Asplund fiber, a pulp produced by the mechanical disintegration of chips under a steam pressure of several atmospheres, but the commercial feasibility of such a treatment has not yet been demonstrated. From a practical standpoint, therefore, it can only be said that a compromise has been reached between economic, technical, and scientific considerations. This compromise calls for the application of the kraft process to take advantage of its low cost and technical feasibility, followed by chlorination to compensate for any heterogeneity in degree of pulping.

4. Steps in Chemical Pulping Common to All Processes

For a better understanding of the material to follow, it is necessary, at this point, to describe briefly the types of wood suitable for pulping and to outline those steps in chemical pulping which are common to all processes. These are: wood preparation, digestion, blowing or dumping, washing, and screening.

(*a*) *Species of Wood Suitable for Pulping*

Volumes might be devoted to the relative merits of various species of wood, the influence of age, growth rate, habitat, storage conditions, density, springwood : summerwood ratio, decay, and other raw-material variables. For this chapter, however, it may suffice to generalize briefly upon the differences between the two broad classes of trees which supply the pulp

[14] G. J. Hajny and G. J. Ritter, *Paper Trade J.*, **111**, 131 (Nov. 28, 1940).

industry. The first and more important of these is referred to by the wood technologist as a *gymnosperm*, a term based upon the fact that the seeds are borne in a relatively uncovered condition. The wood buyer, however, calls a representative of this class a "conifer," an "evergreen," or a "soft-wood," even though the fruit is not always a cone, the tree is not always green, and the wood is frequently very hard. On a volume basis, the largest proportion of the cells in such a wood are tracheids, *i. e.*, fibers which are 2.5 mm. or more in length. The lignin content is relatively high, from 25 to 35%. The cellulose content (Cross and Bevan) ranges from 55 to 63%. Such species, in general, give a low or medium yield (40 to 47%) of a relatively strong pulp.

The other broad class of pulpwood species is called *angiosperm*, broad-leaved, deciduous, or hardwood, depending upon the property emphasized. The last three terms do not apply to every representative of the class, and their use frequently is a source of confusion. Among the *angiosperms* used for pulping, birch would probably best typify the properties which these terms attempt to describe. The principal fiber elements from the conversion standpoint are the *wood fibers*, narrow elements about 1 mm. long, and the vessels or *tracheae*, shorter elements whose width in some cases nearly equals the length. The lignin content is relatively low, ranging from 17 to 25%. The Cross and Bevan cellulose in the case of aspen, an important pulpwood species, may exceed 65%, and pulp yields of over 50% are commonly obtained in commercial practice. Because of the deficiency in fiber length, the pulp responds less satisfactorily to beating and high strength is not attained, but the same dimensional characteristics impart desirable features of formation, surface, and opacity to printing papers.

(*b*) *Wood Preparation*

The first step in wood preparation is bark removal, although this operation is frequently performed before the wood ever reaches the pulp mill. When such is the case, the logs may be peeled either by hand, using a long-handled chisel-like tool called a spud, or by a motor-driven knife barker. When the logs arrive at the mill in the unpeeled condition, the bark is usually removed by permitting the logs to tumble over each other in a drum barker, a cylindrical device so designed that, as it revolves about its slightly inclined axis, the logs gradually and continuously work from one end to the other. The bark is softened and washed away by means of water, in the form either of a pond in which the drum is partly immersed or of sprays which play upon the logs entering and leaving. In Pacific Coast practice, the logs are too large to be handled in such fashion; instead,

they go to the breakdown mill, where they are slabbed into pieces which are either barked or sent directly to the chipper, depending upon whether they are inner or outer slabs.

From the pulp manufacturer's standpoint, bark has no value except as a fuel. Unless completely removed from the surface of the log and from embedded knots, it causes dirty pulp, especially in the sulfite process.

In order to promote satisfactory penetration of the wood by the cooking liquor, it is necessary to subdivide the wood to such an extent that a reasonably uniform treatment can occur. The extent to which this subdivision should be carried is certainly a function of the natural fiber length; sawdust, for example, is not a suitable raw material for the manufacture of paper pulp because excessive quantities of the fibers have been severed into one or more pieces. Actually, in the case of a wood such as spruce, balsam fir, or hemlock, whose tracheids range in length from 2.5 to 3.5 mm., the effect of chipping upon fiber length does not become significant until the chip length has been reduced to three-eighths inch or less. Before this point is reached, the energy expended in chipping becomes a serious consideration. It is commonly believed that penetration is improved by the shattering effect which accompanies chipping. On the other hand, the work of Green and Yorston[15] suggests that a less drastic means of subdividing the wood might be preferable, at least for sulfite pulping. These investigators found that whenever wood has been subjected to a strong impact, the fibers are peculiarly susceptible to attenuation by acid pulping, although the wood behaves in a normal manner toward alkaline pulping agents.

The chips are screened in order to remove undersize and oversize pieces. The former consume chemical and contribute only debris and, frequently, dirt to the pulp; the latter, if sufficiently oversize, are incompletely penetrated by the liquor, with the result that they remain intact throughout the cooking, blowing, washing, and screening operations.

(*c*) *Digestion*

The screened chips are charged into a digester, whose specifications may equal or exceed the following[16]:

Diameter 17 ft.	Liquor 51,750 gals.
Height 70 ft.	Wood 42.78 cords
Contents 11,660 cu. ft.	Pulp 23.00 tons

[15] H. Green and F. H. Yorston, *Pulp Paper Mag. Can.*, **40**, 244 (1939).

[16] B. Johnsen in *The Manufacture of Pulp and Paper*. 3rd ed., Vol. III, Sec. 4, McGraw-Hill, New York, 1937, p. 61.

The digester must withstand pressures as high as 100 pounds per square inch in the case of the sulfite process, or 130 pounds per square inch in the case of an alkaline cook. To save time and to facilitate packing of the chips, the liquor and wood are usually introduced simultaneously.

(*d*) *Blowing, Dumping, Washing, Screening*

After completion of the predetermined cooking schedule, the digester is discharged, usually under pressure, through the blowline into the blowpit. The pulp is washed to remove unconsumed chemical and the soluble products of the reaction. Knots and shives are removed by screening, first on a centrifugal screen perforated with circular holes, then on a series of flat plates in which are milled slots from 0.008 to 0.025 inch in width, depending upon the quality of the pulp being handled. It is then ready for bleaching, for lapping, or for conversion into paper.

5. The Sulfite Process

The active components of sulfite cooking liquor are sulfur dioxide and a bisulfite. Calcium bisulfite, for economic reasons, is the salt most commonly employed. Although the general concept visualizes the participation of sulfurous acid in the pulping reactions,[17] Beazley, Campbell, and Maass[18] have presented data to indicate that only a small proportion of the sulfur dioxide can exist in this form under actual cooking conditions. The industry expresses the initial liquor concentration in terms of "total," "free," and "combined" sulfur dioxide, according to the following definitions:

Total: the total concentration, whether in the form of sulfurous acid, calcium bisulfite, or dissolved sulfur dioxide.

Free: the amount in excess of that theoretically required to form the monosulfite of the metallic cation present.

Combined: the amount theoretically required to form the monosulfite. The combined is not determined directly, but is calculated by subtracting the free from the total.

In each case, the concentration is reported as "per cent" of sulfur dioxide, but the figure as determined is actually in grams per 100 cc. A typical liquor, as charged to the digester, might have the following composition: total SO_2, 6.0%; free SO_2, 4.8%; combined SO_2, 1.2%. Typical *p*H values are 2.2 at the start of the cook, and from 0.8 to 1.5 at the end.

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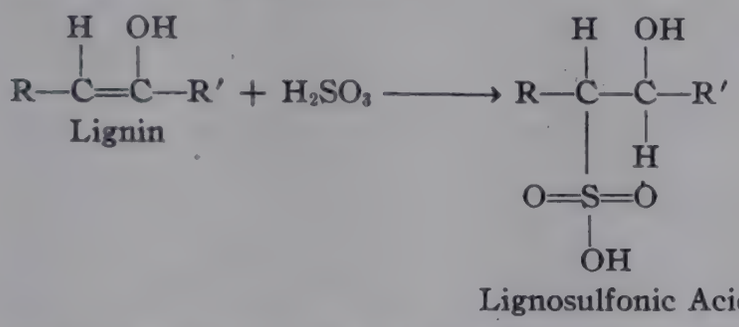
[17] Miller, Swanson, *et al.*, *Chemistry of the Sulfite Process*, p. 101; see ref. 8, p. 481.

[18] W. B. Beazley, W. B. Campbell, and O. Maass, *The Physical Properties of Sulfite Liquors*. Canada Dept. of Mines and Resources, Lands, Parks, and Forests Branch, Dominion Forest Service, *Bull.* **93**. Ottawa, 1938.

A typical ratio of liquor to oven-dry wood might be 4.5 cc. per gram, from which the following chemical ratios have been calculated (expressed on the basis of oven-dry wood): total SO_2, 27.0%; free SO_2, 21.6%; combined SO_2, 5.4%. The ratio for combined sulfur dioxide corresponds to a calcium oxide : wood ratio of 4.7%. In other words, for every 100 g. of oven-dry wood, 27 g. of sulfur dioxide, 4.7 g. of calcium oxide, and about 450 g. of water are employed, in addition to the water in the chips, which might be another 100 g. This represents a total of 685 g., of which approximately 550 g. is water.

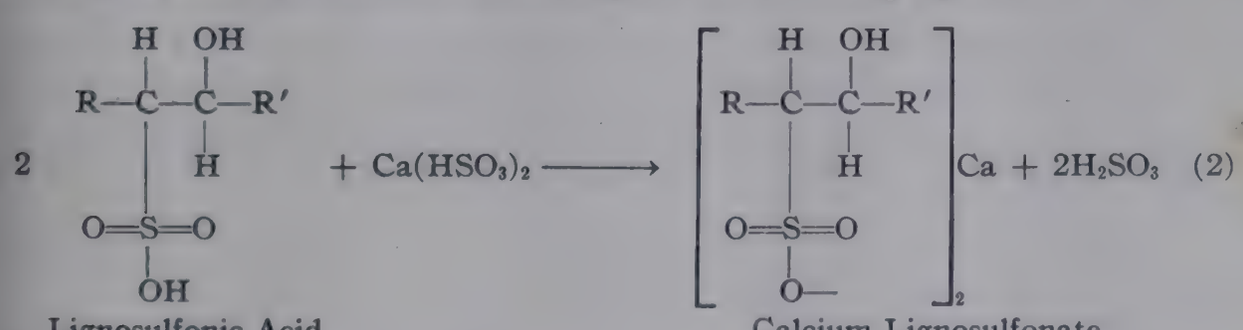
(*a*) *Primary Reactions*

Theories. According to Hägglund and Carlsson,[19] Brauns,[20] and Brauns and Brown,[21] a probable reaction of sulfite pulping is the addition of sulfurous acid to an enolic double bond in the lignin molecule. This may be expressed by the following equation:



(1)

The lignosulfonic acid thus formed is not immediately soluble but, as the digestion temperature is increased, it is hydrolyzed into aggregates which are at least capable of colloidal dispersion in the cooking liquor. According to Brauns and Brown,[21] a rearrangement of the sulfonic group, with the participation of a hydroxyl group, is responsible for the solubilizing of the lignin. The lignosulfonic acid is said to be stronger than sulfurous acid and reacts with the bisulfite according to the following equation:



(2)

[19] E. Hägglund and G. E. Carlsson, *Biochem. Z.*, **257**, 467 (1933).
[20] F. E. Brauns, *Paper Trade J.*, **111**, 33 (Oct. 3, 1940).
[21] F. E. Brauns and D. S. Brown, *Ind. Eng. Chem.*, **30**, 779 (1938).

For every sulfonic acid group which is neutralized, one molecule of sulfurous acid is liberated. Since there is no net increase or decrease in its concentration, the sulfurous acid might, in one sense, be considered a catalyst of the over-all reaction; it is apparent, however, that the sulfite radical in the product of reaction (2) was evolved from the calcium bisulfite, not from the sulfurous acid which entered into reaction (1).

Although it is beyond the scope of this chapter to present a historical account of the chemical pulping processes, no discussion of the sulfite process would be complete without mention of its inventor, Benjamin C. Tilghman,[22] an American chemist who, in 1867, was granted a patent on a method of cooking wood with a solution of sulfur dioxide, with or without the addition of a bisulfite. The first useful theory of the reaction mechanism, however, was advanced by Klason,[23] who believed it to involve the addition of a bisulfite to ethylene groups of the lignin molecule, forming soluble calcium salts of lignosulfonic acid. Hägglund[24] assumed that, in the cooking process, an insoluble compound of carbohydrates and calcium salts of lignosulfonic acid is formed which, at higher temperatures, is hydrolyzed, forming a soluble calcium salt of lignosulfonic acid, and soluble sugars. Miller and Swanson[25] emphasized the hydrolytic action of the cook even more strongly, and at first viewed the sulfite process essentially as an acid hydrolysis of wood. Later, however, these authors felt that the removal of lignin was the result of a specific action of ionized sulfurous acid, and that the simultaneous hydrolytic removal of carbohydrate material was fortuitous; they did not subscribe to the theory that lignin is chemically combined with the carbohydrates in the wood.[26] Beazley, Campbell and Maass[18] disagreed strongly with the hydrolysis theory of Miller and Swanson; on the basis of the dissociation constants of sulfurous acid as a function of temperature, they maintained that the acidity of the liquor is so low under the actual conditions of the cook that hydrolysis of the carbohydrates is minimized. In spite of the lack of complete agreement among these schools of thought represented by Hägglund (*Institut für Cellulosetechnik und Holzchemie* in Stockholm), Miller and Swanson (formerly of the United States Forest Products Laboratory), and Beazley, Campbell, and Maass (Forest Products Laboratories of Canada), these

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[22] B. C. Tilghman, U. S. Patent 70,483 (1867).

[23] P. Klason, *Ber.*, **53B**, 706, 1864 (1920).

[24] E. Hägglund, *Papier-Fabr.*, **24**, Tech.-wiss. Tl., 775 (1926); **27**, Tech.-wiss. Tl., 165 (1929).

[25] Miller, Swanson, *et al.*, *Chemistry of the Sulfite Process*, p. 68; see ref. 8, p. 481.

[26] Miller, Swanson, *et al.*, *Chemistry of the Sulfite Process*, p. 89; see ref. 8. p 481.

research centers must be given credit for much of our present understanding of the sulfite process, from both the scientific and the technological points of view.

Kinetics. In a series of papers, Maass and his coworkers have described some exhaustive studies of the kinetics of the sulfite pulping reactions. Corey and Maass[27] found delignification rates to be in only approximate agreement with the laws for monomolecular reactions. The change in rate of delignification with temperature, however, obeyed the equation of Arrhenius. Calhoun, Yorston, and Maass[28] studied the effects of sulfite liquor composition on the rate of delignification of sprucewood and the yield of pulp. They established a quantitative relationship between rate of delignification and the partial pressure of sulfur dioxide gas. The product of the concentrations of hydrogen and bisulfite ions was found to be the major rate-controlling factor. The yield of pulp for any given lignin content was independent of the free sulfur dioxide concentration but increased markedly with the concentration of the combined sulfur dioxide.

"Burning." The phenomenon of "burning" at the beginning of the sulfite cook is usually associated with the appearance, in the discharged pulp, of chips partially pulped on the outside, but darkened or almost charred on the inside. An investigation by De Montigny and Maass[29] demonstrated that the presence of sufficient base *in the chip* definitely eliminates all danger of burning, irrespective of the rate of heating. These workers attributed the effect of the base to its action in controlling the hydrogen-ion concentration of the cooking liquor, preventing its increase to a point which would result in the polymerization of the sulfonated lignin. It is known that sulfurous acid alone, at temperatures above 110°C., will so alter the lignin that it will not dissolve,[30] although it is true that wood can be pulped in the absence of any base if the temperature is kept below this critical value. Since the free sulfur dioxide penetrates at a much faster rate than does the combined, it is necessary in commercial operation to allow for the penetration of the combined sulfur dioxide into the interior of the chips before the critical temperature is exceeded.

Calcium Sulfite Precipitation. Upon heating sulfite cooking liquor in

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[27] A. J. Corey and O. Maass, *Can. J. Research*, **14B,** 336 (1936).

[28] J. M. Calhoun, F. H. Yorston, and O. Maass, *Can. J. Research*, **15B,** 457 (1937); **17B,** 121 (1939).

[29] R. DeMontigny and O. Maass, *Investigation of the Physico-Chemical Factors Which Influence Sulfite Cooking*. Canada Dept. of the Interior, Dominion Forest Service, *Bull.* **87,** Ottawa, 1935.

[30] Miller, Swanson, *et al.*, *Chemistry of the Sulfite Process*, p. 104; see ref. 8, p. 481.

the absence of wood, a precipitate of calcium sulfite forms. Beazley, Campbell, and Maass[18] explain this fact on the basis of the equilibria in the system calcium oxide–sulfur dioxide–water as influenced by temperature. The principal reactions are expressed by the equation

$$\begin{array}{l} Ca(HSO_3)_2 \leftrightarrows CaSO_3 + H_2SO_3 \\ \qquad\qquad\qquad\qquad\quad \updownarrow \\ \qquad\qquad\qquad\qquad\quad SO_2 + H_2O \end{array} \qquad (3)$$

As the temperature increases, the sulfurous acid tends to decompose into sulfur dioxide and water. The resulting decrease in its concentration causes the first equilibrium to shift to the right, with the formation of dissociated calcium sulfite. Eventually, the solubility product of calcium and sulfite ions is exceeded, and calcium sulfite precipitates. The danger of precipitation is thus an added reason for limiting the digester temperature until the base has penetrated to the interior of the chips, where its major functions must be performed. The system has a strong tendency toward supersaturation, and the presence of colloidal matter derived from the wood inhibits precipitation during an actual cook. For this reason, and because the concentration of calcium ions has decreased appreciably before the theoretical precipitation temperature is reached in commercial operation, precipitation is usually not an unavoidable problem. The importance of the temperature schedule is obvious, however, and one can readily understand why Miller and Swanson[31] found temperature to be the most important single variable in sulfite pulping.

Conductivity of Sulfite Liquor. Van Nostrand,[32] employing conductivity measurements, found that calcium lignosulfonate is dissociated only to a small extent. In order to account for the relatively high conductivity of sulfite waste liquor, he suggested that the reaction between lignosulfonic acid and calcium bisulfite may be reversible. The addition of sulfur dioxide to a calcium lignosulfonate solution raised its conductivity to a value higher than would be expected on the basis of the conducting power of the separate components. Accordingly, it appeared that some free lignosulfonic acid might always be present in the liquor after the cook had progressed to an appreciable extent.

Degradation. It has already been mentioned that, while the solution of the lignin is in progress, an acid hydrolysis of the hemicelluloses is also taking place, resulting in the formation of units whose chain lengths are sufficiently reduced to permit solution. Furthermore, the cellulose itself is degraded to some extent, as is evidenced by the fact that its final

[31] Miller, Swanson, *et al.*, *Chemistry of the Sulfite Process*, p. 63; see ref. 8, p. 481.

[32] R. J. Van Nostrand, Inst. of Paper Chemistry, unpublished work, 1941.

cuprammonium viscosity is always lower than that of cellulose prepared from the same raw material under less drastic conditions.[33]

This is an elementary and somewhat hypothetical picture of the primary sulfite pulping reactions. However, if taken in conjunction with the concept of the chip as an aggregate of several million connected capillaries, each having a fairly definite but chemically heterogeneous wall structure, it may serve as a basis for the technological material which is to follow.

(*b*) *Relieving Sulfur Dioxide Pressure*

At present it is not feasible to construct sulfite digesters capable of withstanding high pressures; hence, it is necessary to begin relieving sulfur dioxide pressure long before the maximum temperature is reached. This gas is recovered by passing the relief through weak cooking acid, which fortifies the latter for a subsequent cook. It may well be asked what is the virtue of carrying this unused sulfur dioxide in the system, since ostensibly it only creates an additional operating problem. It has been found in practice, and demonstrated by experiment, however, that a reasonably high free sulfur dioxide concentration is essential to the promotion of a satisfactory reaction rate. Furthermore, it is a general belief that a high "free" concentration facilitates the penetration of the cooking liquor.[30] Both these functions are performed before maximum temperature is reached; *i. e.*, before all the surplus sulfur dioxide has been relieved.

An hour or two before the end of the cook, a more vigorous relief is begun. This reduces the pressure to a point which will permit blowing without damage to equipment and without serious mechanical harm to the fibers. It also accomplishes the important operating objective of recovering the major portion of the sulfur dioxide which is not consumed by the several reactions. In practice, it is possible to recover the equivalent of the "total" minus twice the "combined" which means that only the equivalent of the sulfur dioxide theoretically present as the bisulfite has permanently entered into the sulfonation reaction. This is in excellent agreement with Equation (2).

(*c*) *Changes in Liquor Composition During the Cook*

In an investigation of the coloring matter of sulfite waste liquor, Simerl[34] has obtained valuable data on the composition of the liquor during the course of the cook. Figure 3 presents typical curves for the total sulfur

[33] W. G. Van Beckum and G. J. Ritter, *Paper Trade J.*, **109,** 107 (Nov. 30, 1939).

[34] L. Simerl, *Tech. Assoc. Papers*, Ser. **23,** 114 (1940).

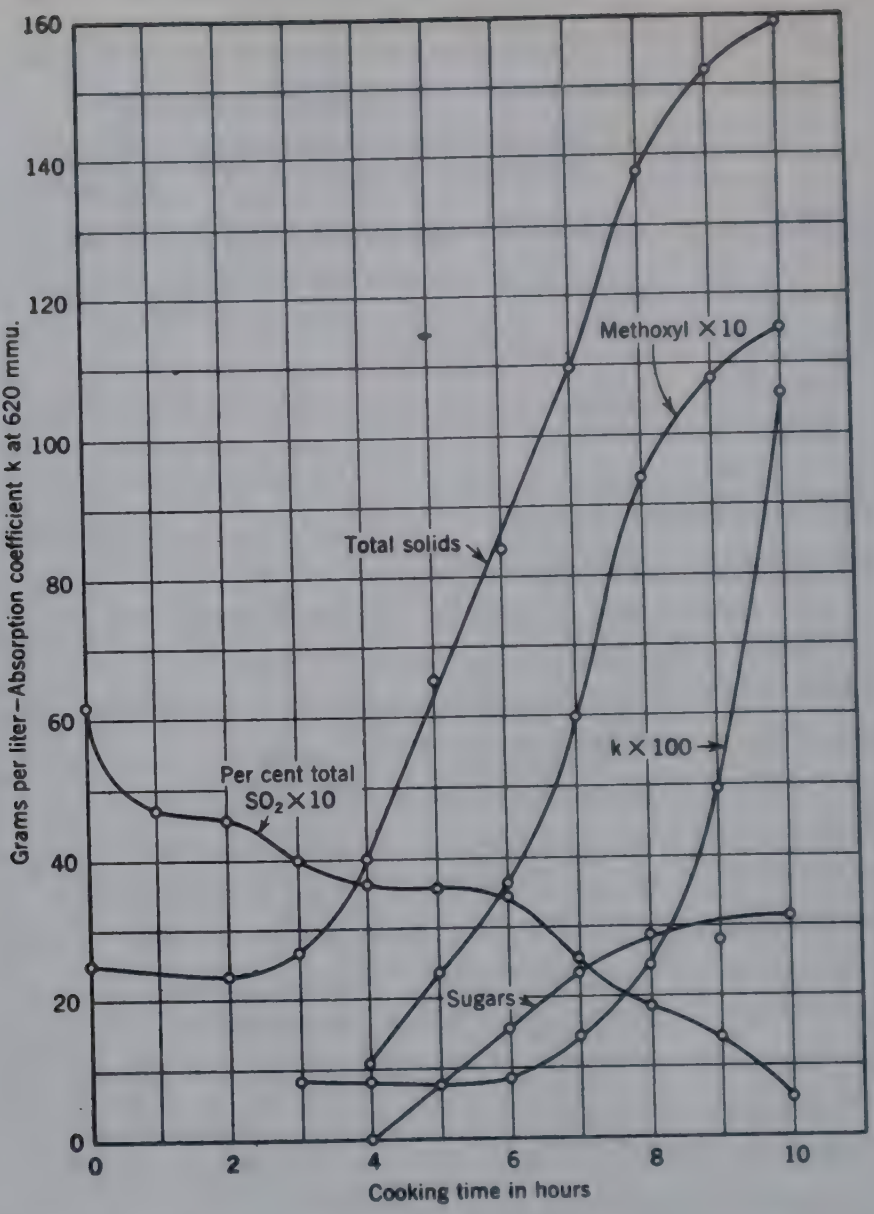

FIG. 3.—THE CONCENTRATION OF CHEMICAL COMPONENTS AND COLORING MATTER AS A FUNCTION OF REACTION TIME IN SULFITE PULPING (SIMERL[84]).

dioxide, total solids, methoxyl, sugars, and absorption coefficient as function of reaction time for a cook made under the following conditions:

Raw material data (average for six logs):

Species	black spruce (*Picea marian*
Age	86 yr.
Diameter	6.0 in.
Density, oven-dry basis	28.6 lb./cu. ft.
Moisture	40%
Chip length	0.75 in.

lfur dioxide concentration:

Total	6.2%
Free	4.8%
Combined	1.2%
iquor : oven-dry wood ratio	3.6 cc./g.
Iaximum temperature	140°C.
ime to 110°C	3.0 hr.
ime 110 to 140°C	4.0 hr.
ime at 140°C	3.0 hr.
Iaximum pressure	75 lb./sq. in.

inear relief to blowing pressure of 50 lb./sq. in. during last hour

Several significant features can be observed from these curves. First, the sulfur dioxide concentration dropped to less than half its original value before maximum temperature was reached. The decrease during the first hour can be attributed largely to losses during introduction and to dilution by the water in the chips. From this point on, however, the decrease was due to relief and, to a lesser extent, the pulping reactions. The methoxyl content, an indication of the lignin present in the liquor, and the total solids increased in a somewhat linear fashion from the fourth hour until the ninth hour, at which time the curves began to flatten. The sugar content increased from practically zero at the fourth hour to 30 g. per liter at the eighth hour, after which it did not change appreciably. The absorption coefficient at 620 mμ, an indication of the depth of liquor color, did not change much until the sixth hour, when it began to develop at a progressively accelerated rate. Because the absorption coefficient curve definitely was not parallel with any of the curves for chemical constituents, Simerl advanced the hypothesis that the final color increase was due largely to carbohydrate degradation, and he later obtained fairly conclusive data demonstrating that such was the case. As one of his conclusions, Simerl stated, "The wood constituents, celluloses, hexosans, and pentosans, hydrolyze to the simple sugars and then break down to form insoluble humus and furfural derivatives. These furfural derivatives condense to colloidal coloring matter and insoluble resins or humic materials, all making up the caramel system."

(*d*) *Reaction Variables*

The contributions of several investigators of the sulfite process have already been mentioned. In view of their excellent work, it might appear unnecessary to present additional data illustrating the effects of the various reaction variables. Nevertheless, such information is submitted on the

following pages for reasons which, at least to the author, appear to be valid. First, technological data on these several reaction variables which have been obtained under reasonably comparable conditions and with the same equipment are somewhat rare. Second, most investigators of sulfite pulping technology have employed experimental conditions which did not depart materially from commercial practice. Although the philosophy of such an approach is sound and commendable, it has resulted in some uncertainty regarding the true influence of the interrelated variables: concentration, temperature, and pressure. In an attempt to eliminate this confusion, several series of experimental sulfite cooks have been performed at The Institute of Paper Chemistry as part of its academic program during the past few years, in which an important departure from commercial conditions has been permitted. Instead of relieving the digester to some arbitrary maximum pressure, the pressure has been made a dependent variable, *i. e.*, allowed to build up to its equilibrium value for the particular conditions of concentration and temperature employed. In this manner, it was felt that a more definite concept of the effects of temperature and free sulfur dioxide concentration could be obtained than would be the case when a variable amount of sulfur dioxide was relieved, depending upon the temperature and pressure specified.

In each series of cooks, three-quarter-inch chips of black sprucewood (*Picea mariana*) were employed. Because the study covered a period of several years, it was impossible to use the same lot of wood as the source of raw material supply, but such variables as age, growth rate, and density were kept reasonably constant. The wood was practically identical with that used by Simerl, except for moisture content.

Liquor analyses were performed according to the method of Palmrose[35]; yield determinations according to standard Institute procedures, before and after screening through a 0.010-inch slotted screen plate; permanganate number,[36] an indication of reducing material, and indirectly of pulping degree, by TAPPI Standard T 214 m-37; and physical strength by Institute methods. The detailed experimental conditions and results are given in Tables 1–4.

The Effect of Free Sulfur Dioxide Concentration. The effects of variation in free sulfur dioxide concentration[37] are shown in Table 1. Since a control series of experiments was performed in which commercial practice was simulated by relieving to a relatively low maximum pressure, consid-

[35] G. V. Palmrose, *Paper Trade J.*, **100**, 38 (Jan. 17, 1935).

[36] Tech. Assoc. Pulp & Paper Ind., *Standards*, **T 214 m-37** (Dec. 15, 1937).

[37] W. G. Hulbert, Jr., Inst. of Paper Chemistry, unpublished work, 1940.

erable information can be deduced regarding the effect of the pressure variable itself by comparing the results of corresponding cooks in the two series.

TABLE 1

SERIES A. NO RELIEF; PRESSURE DEPENDENT

Free SO_2, %	Maximum digester pressure	Total yield, %	Screened yield, %	Lignin, %	$KMnO_4$ no.	Reflectance of pulp at 460 mμ, %	Transmittance of 10-hr. liquor sample at 620 mμ, %
3.01	107.0	49.3	47.0	3.07	16.6	57.8	83.7
4.02	114.0	46.9	45.9	....	13.2	55.2	78.0
4.98	119.5	44.9	44.0	0.59	8.2	62.5	15.0
6.03	140.0	42.6	41.4	0.56	6.6	55.6	1.5
7.00	161.0	40.9	40.7	....	6.5	55.0	0.5

SERIES B. PRESSURE RELIEVED TO PREVENT EXCEEDING MAXIMUM OF 75 LB./SQ. IN.

Free SO_2, %	Time to 75 lb. pressure, hr.	Total yield, %	Screened yield, %	Lignin, %	$KMnO_4$ no.	Reflectance of pulp at 460 mμ, %	Transmittance of 10-hr. liquor sample at 620 mμ, %
3.01	5.75	51.4	44.6	5.14	20.8	45.0	87.5
4.00	5.00	48.5	46.1	....	15.4	51.0	85.5
5.00	3.50	47.6	46.2	3.47	14.2	57.6	84.0
6.01	3.00	47.2	46.3	1.57	14.2	54.5	84.0
7.01	2.75	46.2	45.1	1.47	14.0	49.5	83.5

Constant conditions:

Species: Black spruce (*Picea mariana*)
Combined SO_2 concn. 1.20%
Liquor: oven-dry wood ratio 5.3 cc./g.
Maximum temperature 140°C.
Time to 110°C. 3.0 hr.
Time from 110 to 140°C. 4.0 hr.
Time at 140°C. 3.0 hr.
Moisture content of wood 12%
Linear relief to blowing pressure of 50 lb./sq. in. during last 30 min. of each cook

When no relief was practiced, an increase in the concentration of free sulfur dioxide caused a progressive decrease in the screened and unscreened yield, the percentage of screenings, and the permanganate number. When a fixed maximum pressure was maintained through relief, varying the initial concentrations of free sulfur dioxide (above 4%) had little effect on the yield or permanganate number. This is in agreement with the data of Miller and Swanson.[38] A comparison of the two series shows that cooking without relief resulted in lower yields, less screenings, and lower perman-

[38] Miller, Swanson, *et al.*, *Chemistry of the Sulfite Process*, p. 51; see ref. 8 p. 481.

ganate numbers. In Series A, the trends in strength development agreed with the yield and permanganate number data in indicating a greater severity of the pulping action as the concentration of free sulfur dioxide was increased. Similarly, the difference between the strength characteristics of the two series could be attributed to the higher effective concentration of free sulfur dioxide *throughout* those cooks in which no relief was employed.

Figures 4 and 5 show typical results of liquor analyses made hourly during the cooks of each series. In Figure 4, which represents a cook made without relief and using a liquor initially 6.0% in free sulfur dioxide, it is

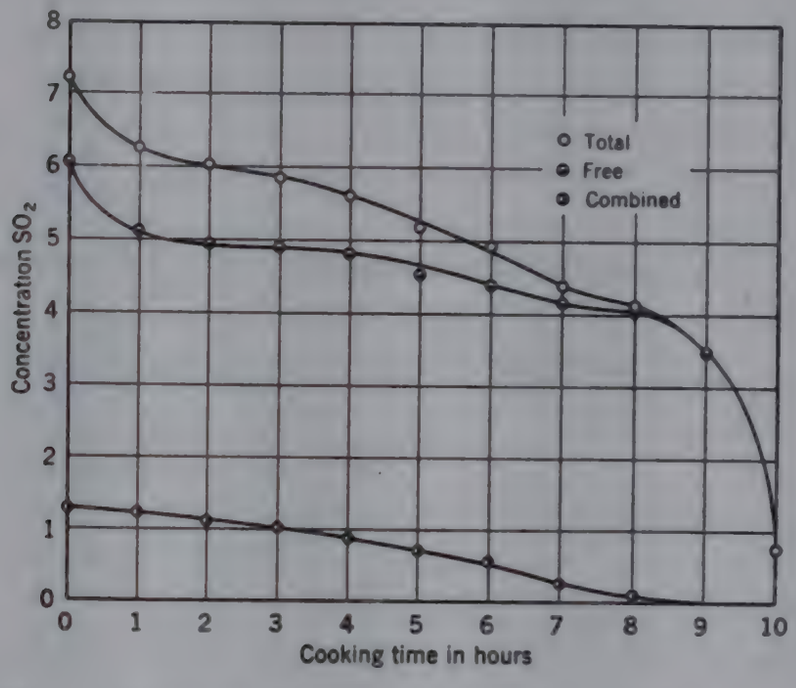

FIG. 4.—SULFUR DIOXIDE CONCENTRATION AS A FUNCTION OF COOKING TIME (HULBERT[87]).

Liquor initially 6.0% in free sulfur dioxide. No relief until blowdown.

seen that the concentration of "excess" sulfur dioxide remained practically constant until the blowdown was begun. This concentration, which is determined by subtracting the per cent combined from the per cent free, represents the sulfur dioxide in excess of that theoretically required to form the bisulfite of the metallic cation present. The fact that its concentration did not decrease is again in accord with Equation (2). When a fixed maximum pressure was maintained through relief, however, the "excess" sulfur dioxide, although not constant throughout any one cook, approached a value which was constant for the series after about six hours of cooking time, regardless of the initial concentration of the cooking acid. The only exception was the cook initially 3.0% in free sulfur dioxide; the "excess"

sulfur dioxide in this case, even after the sixth hour, was definitely lower than was the case for the other cooks of this series.

The disappearance of combined sulfur dioxide in Series B was definitely more rapid for those cooks in which the initial concentration of free sulfur dioxide had been higher, indicating that a greater amount of sulfonation actually had occurred in those cooks.

These facts demonstrate the importance of acid hydrolysis in sulfite cooking. It would seem that sulfonation can be promoted by increasing the initial concentration of free sulfur dioxide; but this increased sulfonation

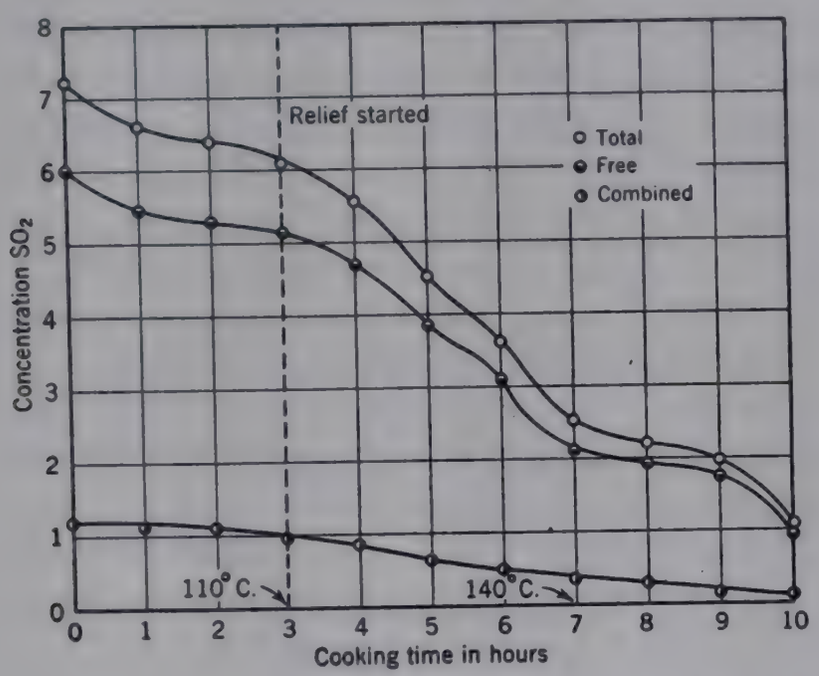

FIG. 5.—SULFUR DIOXIDE CONCENTRATION AS A FUNCTION OF COOKING TIME (HULBERT[37]; *cf.* MILLER, SWANSON, *et al.*[8]).

Liquor initially 6.0% in free sulfur dioxide. Maximum pressure of 75 lb./sq. in. maintained by continuous relief.

has only a minor effect upon pulp yield and pulp quality unless the "excess" sulfur dioxide concentration is maintained at a high level by inhibiting relief, in order to promote the acid hydrolysis of the sulfonated products to soluble aggregates. The individual values for lignin content in Series B do not fit too well into this picture; it should be remarked, however, that the methods available for determining the lignin in well-cooked pulps are very unsatisfactory. The values for light transmittance of the tenth-hour liquor samples were evidence of a progressively increasing acid hydrolysis in Series A, in contrast to a mild and surprisingly constant action in Series B. In each series there was a good correlation between liquor color and pulp permanganate number. In each case, also, the brightness of the pulp

increased to a maximum at 5% free SO_2 and then decreased. These trends can be explained on the basis of progressive purification of the pulp, opposed by a degradation which became predominant at the higher acid concentrations.

In summary, it appears that the "excess" sulfur dioxide concentration has an important influence upon the product variables, liquor color, permanganate number, yield, and brightness, approximately in the order named. Its influence is exerted primarily through the sulfonation reaction, which progresses to a marked degree before maximum pressure is reached, *i. e.*, before the sulfur dioxide concentrations have been affected by top relief. In commercial practice, this effect is partially obscured because the top relief makes the "excess" sulfur dioxide concentration a function of digester temperature and pressure and, hence, practically a constant before maximum temperature is reached, regardless of its initial value. When no top relief is employed, however, the essential conditions are maintained for the acid hydrolysis of the products which have previously been sulfonated, and the influence of the "excess" sulfur dioxide becomes definitely apparent.

The Effect of Combined Sulfur Dioxide Concentration. Chidester[39] prepared a series of sulfite pulps of nearly constant bleach requirement with liquors of progressively increasing combined sulfur dioxide concentration by elevating the temperature to compensate for the decelerating effect of the base. By using a sodium base it was possible to vary the combined sulfur dioxide concentration as desired, whereas precipitation fixes the maximum value at about 1.4% in the case of calcium base liquor. The total sulfur dioxide concentration was constant at 6% and the pressure was not relieved during the cook.

Under these conditions, he found that the yield and strength passed through a maximum when the concentration of combined sulfur dioxide was between 2 and 3%. In order to secure adequate pulping at the higher concentrations, it was necessary to employ temperatures as high as 180°C., which might have accounted for the low yields and inferior strength. On the other hand, the relatively unfavorable results at the lowest concentration might be attributed to excessive hydrolysis resulting from insufficient neutralization of the lignosulfonic acid.

The Effect of Liquor Ratio. The data which appear in Table 2 cover the effects of this variable. As previously mentioned, the experiments were not altogether original, but they do contribute to an understanding of sulfite pulping technology by virtue of the fact that the results were not obscured by the disturbing influence of top relief.

[39] G. H. Chidester, *Paper Trade J.*, **104**, 39 (Feb. 11, 1937).

As will be seen later in the section on alkaline pulping, the normal effect of increasing the ratio of active chemical to wood is a more vigorous pulping action, because it results in a higher effective concentration of the pulping agent at any given interval during the cook. In the series described in Table 2, it is true, the initial concentration of the active chemical agents was constant, except for the small difference in diluting effect by the moisture in the chips. In spite of this fact, the pulping action became progressively more vigorous as the liquor ratio *decreased*. The increase in

TABLE 2

THE EFFECT OF LIQUOR RATIO IN SULFITE PULPING

Liquor: oven-dry wood ratio, cc./g.	Total yield, %	Screened yield, %	$KMnO_4$ no.	Pulp properties at 400 cc. freeness*		
				Beating time, min.	Burst factor, g./cm.²/-g./m.²	Tear factor, 100 g./-g./m.²
7.75	48.2	47.1	11.4	43	68	66
6.0	45.6	44.6	9.5	49	69	70
5.0	44.6	43.4	7.4	55	69	62
4.0	43.9	41.1	6.4	51	62	68
3.0	41.4	36.0	9.5	45	49	45

Constant conditions:

Species: Black spruce (*Picea mariana*)		Maximum temperature	140°C.
SO_2 concn.:		Time to 110°C.	3.0 hr.
Total	6.0%	Time from 110 to 140°C.	4.0 hr.
Free	4.8%	Time at 140°C.	3.0 hr.
Combined	1.2%	Moisture content of wood	17%

* The significance of these properties is given in Section 10, p. 515.

percentage of screenings and in permanganate number at the lowest liquor ratio can be attributed to the fact that the chips were not adequately covered by the liquor in this case. Although the recirculated liquor was continually pumped into the top of the digester above the chip level, the liquor distribution system had not been designed to keep the uncovered chips uniformly wetted. These chips were exposed to the elevated temperature of the steam and to the action of the sulfur dioxide in the vapor phase, without the protective effect of the calcium bisulfite which remained in the liquid phase. As a result, they were badly darkened and incompletely pulped. Although the permanganate number determination was performed on the screened pulp, it is probable that this pulp was seriously adulterated by that portion of the "burned" chips which succeeded in passing through the screen.

Several hypotheses might be advanced to explain the general trend of these experiments. However, since the acid hydrolysis theory again lends itself to the situation as well as any, an attempt will be made to extend its application to these results. According to Hulbert,[37] the excess sulfur dioxide concentration should have remained reasonably constant for the series; the bisulfite concentration, however, must have been depleted more rapidly at the lower liquor ratios, because of its smaller total quantity. Although the total amount of acidic material to be neutralized as a result

TABLE 3

THE EFFECT OF TEMPERATURE IN SULFITE PULPING

Maximum temperature, °C.	Maximum pressure, lb./sq. in. gage	Total yield, %	Screened yield, %	$KMnO_4$ no.	Pulp properties at 400 cc. freeness		
					Beating time, min.	Burst factor, g./cm.²/g./m.²	Tear factor, 100 g./g./m.²
131	99	50.3	43.2	18.2	38	57	57
134	108	47.8	46.2	12.3	38	60	63
137	115	46.5	45.2	11.1	38	57	60
140	127	43.5	41.5	6.9	47	54	63
143	134	41.3	40.8	7.2	45	49	57

Constant conditions:

Species: Black spruce (*Picea mariana*)

SO_2 concn.:

Total	6.2%
Free	5.0%
Combined	1.2%

Liquor : oven-dry wood ratio	4.3 cc./g.
Time to 110°C.	3.0 hr.
Time from 110°C. to maximum	4.0 hr.
Time at maximum temperature	3.0 hr.
Moisture content of wood	31%

of the early sulfonation reactions might have been the same in each cook, its concentration during the period at maximum temperature should have been greater at the lower liquor ratios, not only because of the deficiency in bisulfite, but also *because of the smaller total volume of the liquor in which it was dissolved*. There was sufficient bisulfite, apparently, to prevent the insolubilizing of the lignin, but not to inhibit entirely the hydrolytic effect of the free lignosulfonic acid on the remaining, partially cooked, wood substance. For want of a better term, "autocatalysis" might be applied to this action, indicating that it was the result of materials formed during the cook rather than of any reagent added. Whatever its nature, it undoubtedly occurs in all sulfite pulping; its effect is most readily apparent, however, in a series of experiments such as those just described.

The Effect of Temperature. The data illustrating the effect of this variable are given in Table 3. Although the trends in yield and permanganate number were more pronounced than would be expected in commercial practice, because of the absence of top relief, they support the general observation that temperature is the most important single variable in sulfite pulping.[31] The maximum pressures listed here and in Table 1 help to explain the mechanical problems which would be involved if there were no top relief in a commercial cook.

The Effect of Time at Maximum Temperature. As shown in Table 4, the reactions which occur during the period at maximum temperature are

TABLE 4

THE EFFECT OF COOKING TIME IN SULFITE PULPING

Time at maximum temperature, hr.	Total yield, %	Screened yield, %	$KMnO_4$ no.	Pulp properties at 400 cc. freeness		
				Beating time, min.	Burst factor, g./cm.²/-g./m.²	Tear factor, 100 g./-g./m.²
2.0	56.0	46.3	22.5	40	75	66
2.5	52.6	49.0	18.1	42	73	65
3.0	50.6	47.8	13.9	43	79	68
3.5	48.2	47.1	12.9	49	73	65
4.0	47.4	46.1	14.6	46	72	72

Constant conditions:

Species: Black spruce (*Picea mariana*)		Liquor : oven-dry wood ratio	5 cc./g.
SO_2 concn.:		Maximum temperature	134°C.
Total	6.2%	Time to 110°C.	3.0 hr.
Free	5.0%	Time from 110°C. to maximum	4.0 hr.
Combined	1.2%		

definitely a function of the time allowed for this period. If the period is too prolonged, however, the yield is continually decreased without a corresponding advantage in ease of bleaching as indicated by the permanganate number. As a matter of fact, the determined and qualitatively observed characteristics of the pulp cooked for four hours at maximum temperature were definite indications that the process had been carried slightly too far and that degradation was being accelerated rapidly during the last half hour. In commercial practice it is recognized that the cook must not continue after the exhaustion of the bisulfite if degradation and darkening of the pulp are to be avoided

6. The Soda and Sulfate Processes

(a) *Theory of Soda Process*

The active component of soda cooking liquor is sodium hydroxide. Although in commercial pulping there is always a small amount of sodium carbonate present as a result of incomplete causticizing, this compound has no significant effect upon the nature or speed of the reactions. The following theory of sodium hydroxide pulping is based upon the findings of Brauns and Grimes.[40]

When the wood is placed in the sodium hydroxide solution, it immediately absorbs alkali. The sodium hydroxide probably combines with any free carboxyl or acidic hydroxyl groups that are present in the various components of the wood, but the relatively large amount removed from the solution, even at low temperatures, indicates that much of the alkali is not chemically combined at this stage.

As the temperature rises, the various components commence to diffuse from the chips into the liquor. Probably some material actually dissolves, but for the most part the woody materials diffuse out of the gel structure of the wood in the form of colloidally dispersed particles. The hemicelluloses are further degraded at the maximum temperature of the cook and ultimately form simple water-soluble compounds. Sodium lignate is formed according to the equation:

$$\text{LigOH} + \text{NaOH} \longrightarrow \text{LigONa} + \text{H}_2\text{O} \qquad (4)$$

Assuming that part of the lignin is chemically combined with the carbohydrates, at elevated temperature the sodium lignate breaks away and diffuses out of the chip.

According to the same investigators, "the carbohydrates dissolve very rapidly at the beginning of an alkaline cook, and only after about 20% of the nonligneous part of the wood has been dissolved does the lignin start to disperse at an effective rate. The lignin in the pulp contains less methoxyl as the cooking conditions become more drastic; at the same time the methoxyl content of the product precipitating from the spent liquor rises with more intense cooking conditions."

Brauns and Grimes stated that, for a normal soda cook, the alkali consumption is about 16%, of which approximately 1.5% is used in neutralizing such acid groups as formyl and acetyl. Of the remaining 14.5%, from 3 to 4% is required for solution of the lignin. A part of the remaining

[40] F. E. Brauns and W. S. Grimes, *Paper Trade J.*, **108**, 40 (Mar. 16, 1939).

10.5 to 11.5% is held by the pulp through adsorption, but the major part is used for dissolution of the carbohydrates.

(*b*) *Theory of Sulfate Process*

These generalizations apply also to the sulfate process, at least in a qualitative sense. In the sulfate process, another active pulping agent is present, namely, sodium sulfide; this sulfide is formed by reduction of sodium sulfate with carbon in the chemical recovery operation. The proportion of sodium sulfide in the cooking liquor is expressed in terms of sulfidity, *i. e.*, the amount of sulfide compared to the sum of the sulfide plus the hydroxide, all expressed on a chemical equivalent basis.

Figure 6, taken from Kimble's work,[41] illustrates the changes in color and in chemical composition which occurred in a kraft (sulfate) liquor during an experimental cook made on sprucewood under the following conditions[37]:

Chip length	0.75 in.
Active alkali ratio	27%
Sulfidity	33%
Water : oven-dry wood ratio	5.5 g./g.
Maximum temperature	170°C.
Time to maximum	1.5 hr.
Time at maximum	4.0 hr.

The following yield data were obtained:

Total yield	46.0%
Screened yield	45.7%
Lignin content of screened pulp	3.5%

Ahlm[42] has postulated the reaction:

$$C{=}O + HSNa \longrightarrow C\begin{matrix}OH\\SNa\end{matrix} \qquad (5)$$

which he believes analogous to the addition of bisulfites to the keto group of lignin. Hanson[43] stated that, at cooking temperatures, sodium sulfide is completely hydrolyzed to sodium hydroxide and sodium hydrosulfide, and he further stated that either of these compounds alone will pulp wood.

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[41] G. Kimble, Inst. of Paper Chemistry, unpublished work, 1941; *cf. Paper Trade J.*, **115**, 37 (July 16, 1942).

[42] C. E. Ahlm, *Paper Trade J.*, **113**, 115 (Sept. 25, 1941).

[43] F. S. Hanson, *Paper Trade J.*, **112**, 32 (Jan. 9, 1941).

However, since the work of both Ahlm and Hanson was completed, a question has arisen concerning the purity of the sodium hydrosulfide which they used in their investigations. A more recent experiment, employing a sodium hydrosulfide solution of established purity, has indicated that this compound cannot be classed as a pulping agent in the practical sense

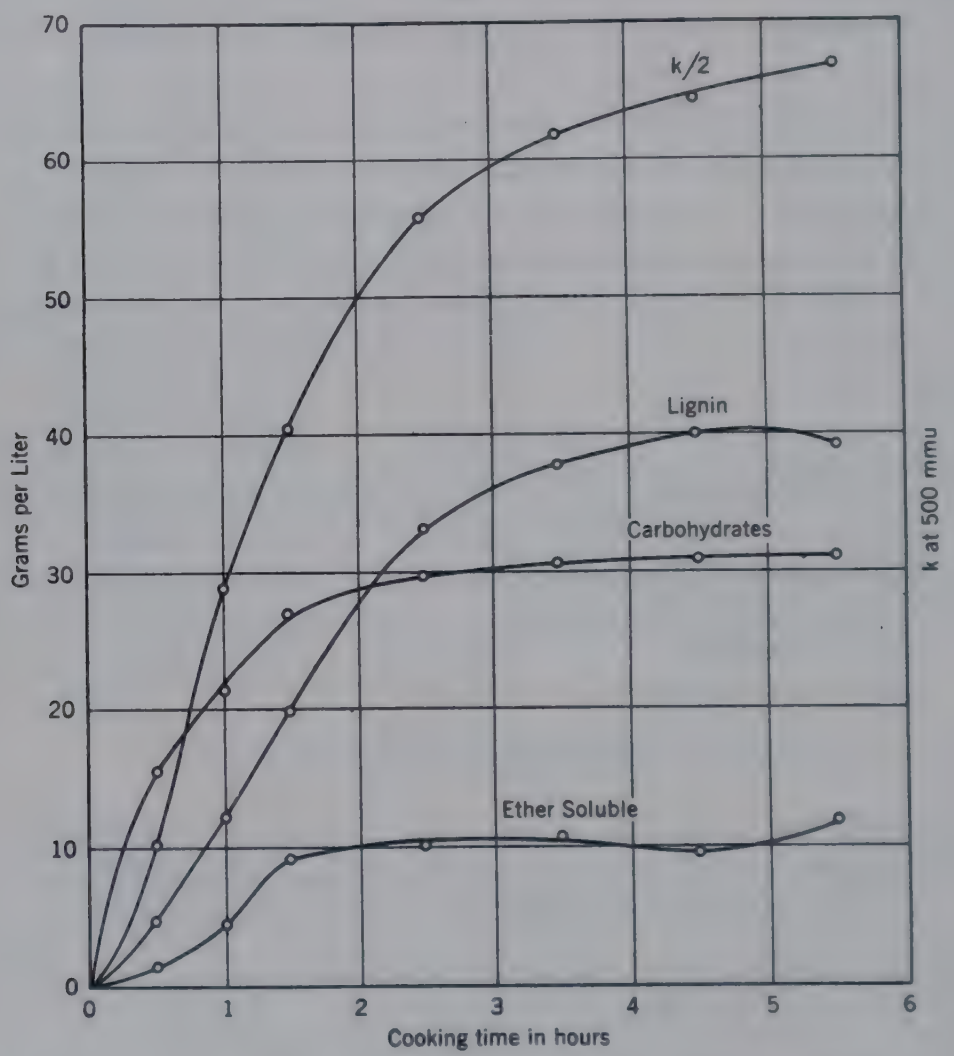

FIG. 6.—CONCENTRATION OF CHEMICAL COMPONENTS AND COLORING MATTER IN SULFATE BLACK LIQUOR AS A FUNCTION OF COOKING TIME (KIMBLE[41]).

of the term, although digestion of spruce shavings with it under severe conditions of concentration, temperature, and time caused a significant loss in weight of the raw material, the removal of about 40% of the lignin in the original wood, and certain changes detectable by the senses of sight and smell.[43a]

The above theoretical background, although admittedly representing

[43a] M. A. Buchanan and C. M. Koon, *Paper Trade J.*, **115**, 116 (Oct. 1, 1942).

the opinions and interpretations of only one school of thought, will be used as the basis of discussion for certain technological data which are to follow.

(*c*) *Reaction Variables*

The Effect of Sulfidity. Data illustrating the effect of this variable under normal conditions are shown in the first three rows of Table 5. As the

TABLE 5

THE EFFECTS OF SULFIDITY AND OF ALKALINITY IN ALKALINE PULPING

Ratio of hydroxide to total chemical, %*	Ratio of sulfide to total chemical, %*	Ratio of carbonate to total chemical, %*	Total yield, %	Screened yield, %	$KMnO_4$ no.	Physical properties at 400 cc. freeness		
						Beating time, min.	Burst factor, g./cm.²/g./m.²	Tear factor, 100 g./g./m.²
100	0	0	50.7	41.4	37.9	75	63	89
90	10	0	46.2	45.6	32.0	67	77	115
67	33	0	43.5	43.3	29.3	73	82	117
67	20	13	47.4	46.5	36.0	80	82	112
67	10	23	48.9	36.9	37.2	85	74	110
67	5	28	54.7	16.0	38.2	78	61	98
67	0	33	58.2	1.5	40+	..	..	..

Constant conditions:

Species: Loblolly pine (*Pinus taeda*)		Water : oven-dry wood ratio	6.0 g./g.
Chip length	0.75 in.	Maximum temperature	170°C.
Chemical ratio, expressed as NaOH (sum of hydroxide plus sulfide plus carbonate)	24%	Time to maximum	1.0 hr.
		Time at maximum	3.0 hr.

* On a chemical equivalent basis.

sulfidity was increased from 0 to 33%, the total yield and the permanganate number decreased; the screened yield passed through a maximum. If the sulfidity had been increased still further, as indicated by the data of Kress and McGregor,[44] a minimum would have been observed in the curves for total yield and permanganate number at about 33% sulfidity.

Bray, Martin, and Schwartz[45] showed that sulfidity could be increased almost indefinitely as long as the total amount of sodium hydroxide, representing the sum of that added as such plus that formed through hydrolysis of sodium sulfide, was kept above a certain minimum.

[44] O. Kress and G. H. McGregor, *Paper Trade J.*, **96**, 40 (June 15, 1935).

[45] M. W. Bray, J. S. Martin, and S. L. Schwartz, *Paper Trade J.*, **109**, 40 (Oct. 26, 1939).

Hanson[43] also found that the optimum sulfidity increased as the active chemical ratio was increased. These facts are important to remember in considering any elaborate hypotheses which may be advanced to explain why a ratio of exactly two parts of sodium hydroxide to one part of sodium sulfide is optimum. As a matter of fact, it is fortuitous that this sulfidity is optimum at the active chemical ratio which prevails in commercial practice. In the days when recovery was less efficient, so that large amounts of salt cake had to be added to maintain a sufficient liquor inventory, it also happened that a sulfidity of about 33% normally prevailed. In recent years, however, recovery practice in many mills has become more efficient, less salt cake is added, and the sulfidity drops to 25% or less. This is not serious, for the sulfidity curve is not abrupt, but it can still be said that the objectives of quality and economy are somewhat opposed to each other in this instance.

Writers on the subject have long maintained that the main function of sodium sulfide is that of a buffer or a reservoir of sodium hydroxide, which permits the accomplishment of the necessary degree of pulping without the initial high alkalinity which would be required if sodium hydroxide alone were employed. If this were true, it should be possible to replace sodium sulfide with the salt of some other weak acid, such as carbonic acid. This has been tried, as shown in the last four rows of Table 5. However, as more and more of the sulfide was replaced by carbonate, the degree of pulping became progressively less until, when only hydroxide and carbonate were present, the wood was scarcely defibered. Since the dissociation constants of carbonic acid and hydrogen sulfide are of the same order, it must be concluded that the buffer or reservoir effect is of minor, if not negligible, importance.

Mills which are not equipped for smelting, either because of the installation expense or because of a local ordinance against the kraft odor nuisance, can and often do obtain some of the benefits of sulfidity by adding small amounts of sulfur either to the soda cooking liquor or to the digester charge directly. The following reaction has been proposed[46]:

$$6NaOH + 4S \longrightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O \qquad (6)$$

Because the sodium hydroxide is depleted by the reaction, and because only a part of it is converted to sulfide, even under ideal conditions, there is a limit to the amount of sulfur which should be added. Under typical commercial conditions, little or nothing is gained by adding over 6% of

[46] A. W. Schorger, *The Chemistry of Cellulose and Wood*. McGraw-Hill, New York, 1926, p. 408.

sulfur, based upon the oven-dry weight of the wood. It is the general opinion that the low sulfidity accomplished by this means does not create as much of an odor problem as is encountered in normal kraft operation.

The Effect of Chemical Ratio. A series of sulfate cooking experiments was performed in which the ratio of active chemical (expressed as sodium hydroxide) to wood was varied from 20 to 32%. The detailed conditions and the results are given in Table 6. As would be expected, the total

TABLE 6

THE EFFECT OF CHEMICAL RATIO IN SULFATE PULPING

Chemical ratio as NaOH, %*	Total yield %	Screened yield, %	$KMnO_4$ no.	Chlorine requirement for 78% brightness, %	Physical properties at 400 cc. freeness		
					Beating time, min.	Burst factor, g./cm.²/g./m.²	Tear factor, 100 g./g./m.²
20	45.7	43.6	25.6	8.6	49	54	100
24	43.9	42.0	21.7	8.3	46	55	108
26	42.4	41.6	20.3	6.8	44	54	99
28	40.5	39.8	17.2	6.7	44	50	102
32	38.3	38.1	14.9	5.1	36	47	90

Constant conditions:

Species : Loblolly pine (*Pinus taeda*)		Maximum temperature	176°C.
Chip length	0.75 in.	Time to maximum	1.0 hr.
Water : oven-dry wood ratio	5.0 g./g.	Time at maximum	3.0 hr.
Sulfidity	33%		

* Includes only active alkali, the sum of hydroxide plus sulfide.

yield, screened yield, and the permanganate number progressively decreased throughout the range studied. The total chlorine requirement for bleaching in a three-stage chlorine-alkali-hypochlorite process correlated well with the permanganate number; approximately 0.33% of chlorine was required per permanganate number unit. The data taken as a whole demonstrate well that the ratio of active chemical to raw material, since it controls the active chemical concentration at successive intervals throughout the cook, is of primary influence upon the over-all rate of pulping.

The Effect of Maximum Temperature. Three experiments were performed to illustrate the effect of this variable. As shown in Table 7, a temperature increase in the range from 170 to 180°C. reduced the yield and permanganate number somewhat, but the trend indicated that the effect per degree C. became progressively less at more elevated temperatures.

It has already been mentioned that the reaction rate in alkaline pulping doubles with every 10°C. increase in temperature.[9] In applying this rule, however, it must be remembered that, in commercial operation or in experiments such as those described in Table 7, the concentrations of the compounds participating in the reactions are not controlled as would be the case in an ideal system set up to determine the kinetics of the reaction. This fact explains why a simple relationship between temperature and reaction rate cannot be demonstrated by means of the empirical data presented here.

TABLE 7

THE EFFECT OF MAXIMUM TEMPERATURE IN SULFATE PULPING

Maximum temperature, °C.	Total yield, %	Screened yield, %	$KMnO_4$ no.	Physical properties at 400 cc. freeness		
				Beating time, min.	Burst factor, g./cm.²/g./m.²	Tear factor, 100 g./g./m.²
170	42.1	41.9	17.3	59	78	183
176	38.5	38.4	14.4	58	72	153
180	37.8	37.7	14.3	62	71	144

Constant conditions:

Species: Southern pine (*Pinus sp.*) — Water : oven-dry wood ratio 4.0 g./g.
Chip length 0.75 in. — Sulfidity 33%
Chemical ratio as NaOH 28%

The Effect of Time at Maximum Temperature. Another series of three experiments was performed to demonstrate the effect of this variable. The results, which are given in Table 8, illustrate trends similar to those described for maximum temperature—namely, an increase in the degree of pulping for the early increments, and a rapid decrease in the effect with successive increments. These data are in accord with the curves of Figure 6 showing the concentration of the liquor components as a function of time. The falling off of the reaction rate with continued cooking can be attributed to the decrease in the concentration of the reactants and perhaps, also, to the increase in the concentration of the products.

Unless the concentration of the active pulping agents is maintained at a reasonably high value, neither maximum temperature nor time is a very effective means of controlling the extent of the reactions.

The Effect of Water Ratio. These data are given in Table 9. As the water ratio was decreased through the range from 7.75 : 1 to 3.5 : 1, the

total yield and permanganate number progressively decreased. The screened yield passed through a maximum. The relationship between permanganate number and chlorine requirement was no longer linear; the

TABLE 8

THE EFFECT OF COOKING TIME IN ALKALINE PULPING

Time at maximum temperature, hr.	Total yield, %	Screened yield, %	$KMnO_4$ no.	Physical properties at 400 cc. freeness		
				Beating time, min.	Burst factor, g./cm.²/-g./m.²	Tear factor, 100 g./-g./m.²
1.0	50.5	47.9	37.5	85	124	128
2.0	47.9	47.2	22.1	79	115	144
3.0	45.0	44.8	20.4	81	110	149

Constant conditions:

Species: Spruce (*Picea sp.*)		Sulfidity	33%
Chip length	0.75 in.	Maximum temperature	176°C.
Chemical ratio as NaOH	20%	Time to maximum	1.0 hr.
Water : oven-dry wood ratio	4.0 g./g.		

TABLE 9

THE EFFECT OF WATER RATIO IN SULFATE PULPING

Water: oven-dry wood ratio, g./g.	Total yield, %	Screened yield, %	$KMnO_4$ no.	Total chlorine for 78% brightness, %	Physical properties at 400 cc. freeness		
					Beating time, min.	Burst factor, g./cm.²/-g./m.²	Tear factor, 100 g./-g./m.²
7.75	45.6	40.9	30.7	19.0	49	71	100
6.0	43.8	42.7	29.5	14.2	59	73	99
4.5	43.0	42.7	26.6	12.4	51	66	100
4.0	42.5	42.2	25.3	9.3	57	66	96
3.5	40.1	39.6	21.9	8.8	50	72	85

Constant conditions:

Species: Loblolly pine (*Pinus taeda*)		Maximum temperature	170°C.
Chip length	0.75 in.	Time to maximum	1.5 hr.
Chemical ratio as NaOH	24%	Time at maximum	3.5 hr.
Sulfidity	33%		

rapid increase in chlorine demand per permanganate number unit with increasing rawness of the pulp is characteristic in the range from 25 to 40 permanganate number. The results of this series of experiments point to

active chemical *concentration* as an important variable in the cooking process.

7. Comparison of the Chemical Pulping Processes

To recapitulate, the sulfite process, it is believed, is based upon the addition of sulfurous acid to an enolic double bond in the lignin molecule, followed by hydrolysis of the lignosulfonic acid into aggregates which are at least capable of colloidal dispersion in the cooking liquor. In order to prevent the insolubilizing of the lignin and excessive hydrolysis of the carbohydrates, a bisulfite is employed, which converts at least part of the lignosulfonic acid into the corresponding salt. It appears that an equilibrium is established and that both the acid and its salt are present in the liquor during the latter stages of the cook. The carbohydrate portions of the wood hydrolyze to simple sugars, the extent of this hydrolysis depending upon the resistance of the original carbohydrate fraction. The cellulose is the most resistant and, consequently, is least degraded. The end products of the carbohydrate degradation are related to the humic substances; furfural derivatives are formed as intermediate products. The various phases of the above lignin and carbohydrate reactions proceed more or less simultaneously and it is probable that compounds representing every step could be found either in the spent liquor or in the pulp.

In the soda process, sodium hydroxide reacts with acidic hydroxyl groups in the lignin and with various organic acids present in the wood. A large portion of the base, however, is required for removal of the simpler carbohydrates. These dissolve very rapidly at the beginning of an alkaline cook, and only after about 20% of the nonligneous part of the wood has been dissolved does the lignin start to disperse at an effective rate.

In the sulfate process, sodium hydrosulfide derived from hydrolysis of sodium sulfide reacts by addition to a keto group of the lignin molecule. It is believed that the product, which may be considered a sodium salt of thiolignin, is more readily soluble in the cooking liquor than is the original lignin.

As an example of recent European opinion on this subject, the following quotation from an article by Jayme[47] may be cited:

> The sulfite digestion of wood produces easy bleaching pulps of light color and high chemical purity in satisfactory yield. For this reason, rayon pulps, on which severe demands with respect to their content of pure, alkali-resistant cellulose are made, were

[47] G. Jayme, *Papier-Fabr.*, **38**, 277 (1940).

produced by this process exclusively. It is so capable of transformation that pentosan-rich materials, such as beechwood, can be digested to yield pulps poor in pentosans.

On the other hand, the sulfite process has certain disadvantages, such as the less satisfactory cleanness of the pulp, which necessitates careful sorting of the wood; moreover, it is impossible to recover the spent liquors completely. Accordingly, the reproach has been brought against the sulfite process in increasing measure that it compares unfavorably with the sulfate cook as regards the disposal of waste liquor. If the waste liquor is not burned (a problem which has not been satisfactorily solved from the economic side), stream contamination results, and recently built plants have experienced all sorts of troubles because of this question. Moreover, when beechwood is cooked, alcohol cannot be recovered from the waste liquor as the pentoses formed from the pentosans yield no alcohol on fermentation. To be sure, recent studies which use the yeast *Torula utilis* for the production of fodder yeast from waste sulfite liquors suggest a new possibility, but this does not alter the total picture of waste liquor disposal, as the problem of the quantitative utilization of lignin sulfonic acids in the waste liquor still awaits a solution. The possibility of the production of tannins and vanillin is still too slight to have any effect. The greater part still goes into the river.

On the other hand, the waste liquor question is much more satisfactory in the case of the sulfate cook as the organic substances in the black liquor are burned in the course of alkali recovery and are thus utilized at least as a source of heat. The necessary equipment is well built and has long proved satisfactory. The pulp produced in the sulfate cook is cleaner, for the impurities contained in the wood are better dispersed by the alkaline liquors, or more completely dissolved. When resinous woods are cooked, turpentine and "sulfate oil" are obtained in large amount as valuable by-products. Sulfate pulp is also characterized by high strength, which is scarcely obtainable by the sulfite process.

On the other hand, disadvantages of alkaline digestion are the darker color of the pulp and the difficulty of obtaining a satisfactory bleach. In general, sulfate pulp is not only richer in lignin than sulfite pulp but is also especially hard to bleach—probably because of the formation of sulfur-containing coloring matters. Accordingly, bleaching processes have been developed abroad which give a satisfactory white content in from five to seven steps. However, according to samples at our disposal, the white content is not so high as that of bleached sulfite pulp and has a maximum value of 85%, while good rayon sulfite pulps have a white content of 92% as compared with baryta white.

From the chemical viewpoint, the sulfate cook gives pulps which, although obtained in satisfactory yield, contain much more pentosans than sulfite pulps. This fact is of especial importance in the case of starting materials of high pentosan content, such as deciduous woods, bamboo, straw, sunflowers, and other annuals. Of course, a certain change can be brought about by varying the composition and concentration of the cooking liquor, but the forcing of a lower pentosan content is always associated with a much greater decrease in yield.

8. The Removal of Hemicelluloses from Wood by Chemical Pulping Processes

The term hemicellulose is defined by most writers as those noncellulosic carbohydrate constituents of the cell wall which are soluble in dilute alkalies

but not in water, and are readily hydrolyzed by dilute acids.[48] In many cases, however, this definition is not altogether applicable. For example, the soda and sulfite pulping processes, without too great a stretch of the imagination, might be described as treatments of wood with a dilute alkali and a dilute acid, respectively, and yet these treatments frequently do not remove over half of the pentosans originally present in the wood. Straw cellulose cannot be freed from xylan by the action of alkali until all the lignin has been removed.[49] It would seem, therefore, that the practice of Lewis and Davis,[50] who use "hemicellulose" as a group term for the noncellulosic carbohydrates of the cell walls of the wood, is preferable because it entails less confusion.

Probably the most extensive study of the behavior of hemicelluloses during sulfite pulping is that of Zherebov,[51] who cooked a hemicellulosic fraction, derived from aspenwood, with typical sulfite liquors and with sulfurous acid alone. Zherebov's conclusions in part were as follows:

"On being heated with cooking acid above 80°C., pentosans form a compound with calcium bisulfite in which one molecule of the bisulfite is attached to a pentosan molecule consisting of four pentose units. On raising the temperature to 136°C., a more stable compound is formed, in which one molecule of calcium bisulfite is combined with two pentose remnants. As the temperature is raised above 136–137°C., a rapid decomposition of the compound $Ca(C_5H_8O_4.SO_2)_2$ occurs. Free sulfurous acid without bisulfite reacts more rapidly than does the bisulfite; however, when bisulfite is present, its combination with the pentosans precedes the reaction with free sulfur dioxide."

As Zherebov himself points out, however, these conclusions should be applied to actual wood digestion with care. In the first place, the carbohydrate fraction which he used did not comprise the entire hemicellulosic portion of the aspenwood, and, even if it had, it would not have been representative, necessarily, of the behavior of gymnosperm hemicellulose. In actual pulping, the presence of lignin, cellulose, and the products of lignin sulfonation reactions would be expected to repress some of the reactions described and to give rise to other reactions of a considerably

[48] A. G. Norman, *The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.* Clarendon Press, Oxford, 1937, p. 37. See also Chapter IV of this Vol. V of the High Polymer series, pp. 425–46.

[49] E. Heuser and A. Haug, *Z. angew. Chem.*, **31**, 166 (1918).

[50] H. F. Lewis and H. L. Davis in E. Sutermeister's *Chemistry of Pulp and Paper Making*. 3rd ed., John Wiley, New York, 1941, p. 9.

[51] L. P. Zherebov, *Bumazhnaya Prom.*, **6**, No. 7 387 (1927); *Paper Trade J.*, **86**, 55 (Feb. 9, 1928).

different nature. For these various reasons the results observed by Zherebov should be considered as representing reactions which are possible in actual practice but which do not always go to completion except under extreme conditions. The trends observed by Simerl,[34] which have already been quoted, are probably more typical of normal conditions.

The behavior of hemicelluloses in alkaline pulping is no less obscure than in sulfite. According to Brauns and Grimes[40] about half of the alkali consumed is used for dissolution of carbohydrates, but the mechanism of the process has not been definitely established. These investigators felt that the hemicelluloses diffuse out of the gel structure of the wood in the form of colloidally dispersed particles which are further degraded at the maximum temperature of the cook and ultimately form simple water-soluble compounds.

According to Bray and Andrews,[52] "The pentosan content of aspenwood is rapidly reduced from 18.7 to 7.7%[53] during the first hour of cooking at maximum pressure. Beyond this point the pentosan content remains practically constant. This minimum value is reached at the time that the maximum purity of the pulp is attained. Although the pulps contain over 97% cellulose,[54] they show a content of over 7% pentosans. This indicates that pentosans are present in at least two forms: one readily removed from the cellulose nucleus by hydrolysis, and the other held in more stable combination with the cellulose."

According to Schorger,[55] the sulfite process removes more pentosans than do the alkaline processes. However, it would be impossible to state from the pentosan content of a pulp that it had been made by a certain process without knowing the nature of the raw material. A sulfite pulp from a hardwood contains about the same amount of pentosans as a coniferous pulp made by an alkaline cook. Unbleached Mitscherlich sulfite pulp is high in pentosan content in comparison with a sulfite pulp prepared from the same raw material under more drastic conditions.

The behavior of some commonly pulped species under normal experimental conditions is illustrated in Table 10. The process variables were the same for all the sulfite cooks; for the alkaline cooks the only process variable which was not constant within the series was the sulfidity, which was zero in the soda cooks and 33% in the kraft cooks.

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[52] M. W. Bray and T. M. Andrews, *Paper Trade J.*, **76**, 49 (May 10, 1923).

[53] All results were calculated on the basis of the original oven-dry wood weight.

[54] The authors quoted have reference to cellulose as determined by the Schorger method, described in *Ind. Eng. Chem.*, **9**, 556 (1917).

[55] A. W. Schorger, *The Chemistry of Cellulose and Wood*, p. 421; see ref. 46, p. 506.

The most outstanding feature of these results was the high pentosan content of the alkaline hardwood pulps, and the correspondingly low values for the percentage removal of pentosans based upon the analysis of the raw material. The soda process consistently removed a higher proportion of pentosans from both the hardwoods and the softwoods than did the kraft process under comparable conditions. The differences between species of a

TABLE 10

REMOVAL OF LIGNIN AND PENTOSANS IN CHEMICAL PULPING

Species	Process	Pulp Analysis		Loss of constituents during pulping	
		Lignin, %	Pentosans, %	Lignin, %	Pentosans, %
Black spruce	Sulfite	1.7	5.1	97	80
Balsam fir	Sulfite	3.1	3.3	96	87
Beech	Sulfite	2.3	7.2	96	86
Basswood	Sulfite	3.6	7.4	93	85
Jack pine	Soda	7.2	6.1	89	80
Jack pine	Kraft	2.9	7.4	94	75
Western hemlock	Soda	6.3	3.0	91	86
Western hemlock	Kraft	3.1	7.1	96	67
Aspen	Soda	1.9	15.3	94	63
Aspen	Kraft	1.5	18.0	95	52
White birch	Soda	2.0	18.7	96	65
White birch	Kraft	2.1	21.8	96	53

Constant conditions:

Sulfite cooks: As listed in Table 3; maximum temperature 140°C.; maximum pressure 75 lb./sq. in.

Alkaline cooks: As listed in Table 6, except that water ratio was 6:1 and chemical ratio was 24%.

given class were not large. A direct comparison of the sulfite and alkaline pulping results is impossible because, unfortunately, the same species were not pulped by all three processes. However, the data appeared to support the observations of Schorger[55] as far as the hardwoods were concerned; the pentosan contents of the sulfite pulps were much lower. For the coniferous woods, the sulfite and soda processes appeared to remove roughly equal *proportions* of the pentosans originally present; the kraft process, on the other hand, was less effective in pentosan removal.

9. Other Pulping Processes

Although the sulfite, soda, and sulfate processes supply the only important tonnage of chemical pulps, a few other processes might be mentioned.

The Keebra process[56] involves the use of sodium sulfite, or a mixture of sodium sulfite and sodium carbonate. A high yield of strong pulp is obtained, and the pulp can be bleached to a good color; however, the chemical requirement is very high, and no completely satisfactory recovery process has yet been developed.

Wood can be pulped by boiling in nitric acid solution.[57] However, neither the physical nor the chemical properties of the pulp appear to justify the expense of the process at the present time.

Aspen can be pulped with a 50% solution of normal butanol in water.[58] The pulp quality is not exceptionally good, but the by-products obtainable from the liquor are at least of theoretical interest.

The Forest Products Laboratory process, involving alternate treatments with chlorine and a base, has already been mentioned.[14] It is essentially an adaptation of the Cross and Bevan cellulose isolation method.

10. Pulp Strength

Very little has been said thus far about the strength properties of pulp. Unfortunately, although several methods are available for determining such characteristics, and although a great deal of attention has been devoted to each of them, there is no procedure which is completely satisfactory. One or more of the following objections apply to whatever method is chosen: (1) poor correlation with commercial behavior; (2) poor agreement between laboratories and between successive determinations in the same laboratory, particularly over extended periods of time; (3) contamination of sample with inorganic material through abrasion of the pulp-testing device.

The strength data presented in Tables 2 to 9 were obtained according to the Institute method, an adaptation of TAPPI Standard T 200 m-40.[33] The second objection cited above applies particularly to this method, but no better one was available. The occasional inconsistencies in the strength trends illustrated by the tables can be attributed primarily to weaknesses in the testing method.

A statistical interpretation of strength data obtained during experimental pulping investigations over a period of several years indicates a pattern which can be expected in most cases. There are occasional exceptions, and an anticipated maximum or minimum in a strength curve

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[56] Anon., *Paper Trade J.*, **77**, 51 (Sept. 6, 1923).

[57] O. Routala and J. Sevón, *Cellulosechem.*, **7**, 113 (1926).

[58] S. I. Aronovsky and R. A. Gortner, *Ind. Eng. Chem.*, **28**, 1270 (1936).

may be of negligible magnitude in practice, but the general pattern deserves mention if only because of theoretical considerations. The aspects of pulp strength are too numerous to be included in the scope of this chapter, but it may suffice to state that at least three factors must always be considered; namely, the development of bonding between fibers, the reduction of fiber length, and the over-all rate of beating. The beating characteristics in the tables have been selected to represent these three important aspects. The bursting strength of the pulp handsheet depends directly upon the degree of bonding between fibers; the tear is influenced strongly by the fiber length and by the bulk of the handsheet; and the time required for the freeness (drainage rate) to drop to a definite value is an arbitrary but useful indication of the over-all rate of beating.

It has been mentioned previously[5] that the lignin sheath surrounding the fibers as they naturally occur must be removed before satisfactory strength properties can be obtained. After this degree of purification is reached, the beating behavior of the pulp depends upon the relative rates of carbohydrate removal and cellulose degradation. It is generally found that a high hemicellulose content causes a pulp to develop rapidly a high degree of interfiber bonding and to exhibit a rapid drop in freeness.[59] The resulting compactness of the sheet, however, is associated with a relatively low tearing strength. As the degree of pulping is further increased, the product begins to approach alpha-cellulose in its physical behavior; the removal of hemicellulose inhibits the development of interfiber bonding; a free stock is produced and the resulting sheet will have a high bulk and may have a good tear, but always has an unsatisfactory burst. Finally, with an extreme degree of pulping the cellulose itself is damaged to such an extent that the individual fiber has little strength. A slight maximum may be observed in the properties depending upon interfiber bonding due to the adhesive properties of the cellulose degradation products, but the ultimate product upon beating forms a slow stock with neither bursting nor tearing strength.

In this attempt at brevity, the impression must be dispelled that the physical properties of a pulp can be predicted with accuracy from a knowledge of either its chemical analysis or the conditions of its production. This is inevitable, because the various stages described in the preceding paragraph may be in progress simultaneously, although in different portions of the chip or in different regions of the digester. In practice, therefore, the maxima and minima of the strength curves are somewhat obscured by the overlapping of the various reactions, but the influence of

[59] H. E. Obermanns, *Paper Trade J.*, **103**, 83 (Aug. 13, 1936).

these reactions upon physical properties can be identified if a sufficient number of experiments over a sufficiently wide range of conditions are performed.

11. Types of Pulp and Uses

Of all the raw material and process variables affecting the nature of the pulp, species is potentially the most important. Although it is true that variation within a species, state of the raw material, and conditions of pulping markedly affect pulp quality, it is generally impossible so to adjust any of these factors that the inherent differences between one species and another are completely overcome. Furthermore, although certain species can be used almost interchangeably as far as pulp quality is concerned, no amount of adjustment would ever reconcile the differences between spruce and aspen, or between jack pine and birch.

Unbleached spruce sulfite is a pulp of medium strength, which has a desirable color and excellent formation properties. It finds its way largely into mixtures with groundwood in newsprint and other low-cost grades of printing paper.

Bleached spruce sulfite for similar reasons ranks highly among the pulps which are used in white and light-colored papers, such as bond, book, and writings. Specially prepared grades are used to a considerable extent for the preparation of cellulose derivatives.

Prolonged cooking at a relatively low temperature in a special type of digester produces a grade of sulfite known as Mitscherlich. Both unbleached and bleached spruce Mitscherlich sulfite are used largely in the manufacture of glassine papers, because of their easy beating properties. This ease of beating is attributed to the retention in the pulp of a greater proportion of hemicellulosic material as a result of the mild cooking conditions.

Hardwood sulfite, which is used most commonly in the bleached condition, is a pulp of inferior strength, but excellent color and formation characteristics. It is used in admixture with long-fibered pulps to improve the color, formation, and surface texture of high-quality printing, writing, and tissue papers.

Bleached soda pulp from spruce is roughly comparable with bleached spruce sulfite except in respect to color. The sulfite can be bleached to a higher brightness and to a bluer white than can soda pulp. Bleached spruce soda is used primarily in printing papers.

Hardwood soda, which is used only in the bleached condition, is a pulp of low strength, medium brightness, but excellent formation characteristics.

It helps to impart the qualities of good formation, smooth surface, high opacity, and high bulk to printing papers.

Unbleached jack pine kraft (sulfate) has exceptionally high strength, reasonably good formation characteristics, and a light-brown color which is characteristic of all unbleached krafts. It is employed in such grades as wrapping paper, bag paper, and container board, where strength is the important specification.

Bleached jack pine kraft ranks similarly among the white pulps. It is used in all light-colored papers and boards where strength is important, such as envelope, bag, and wrapping papers, white patent-coated board, filing folders, etc.

Hardwood kraft pulp has practically the same properties as hardwood soda and is used for the same purposes.

In addition to the pulps described above, the numerous other pulpwood species, the wide latitude in cooking conditions and degree of bleaching, and the possibility of blending as many as half a dozen pulps in one furnish provide the papermaker with a wide selection of materials for his fabrication. The pulps mentioned, however, represent the most important types of chemical wood pulp.

B. COTTON LINTERS

E. F. HINNER

The discussion of the preparation of cellulose from seed hairs will be confined to cotton, the most useful and most important of all seed hairs. Other seed hairs, such as kapok fiber, milkweed, and the like, are used to a minor extent in nonchemical uses such as in the upholstery industry or other industries where a fibrous and bulky material is required. In the present emergency kapok and milkweed floss,[1] because of their buoyancy, are being used extensively in life preservers and life jackets. Because of its excellent insulating as well as buoyancy qualities, milkweed floss has also been proposed for use in linings for clothing, especially for airplane pilots. Various seed hairs, other than cotton, have been proposed from time to time as sources of chemical cellulose but, due to economic and other reasons, they have not been used commercially in this field.

1. Cotton and Cotton Linters

The two types of hairs which are developed on the cotton seed, as mentioned in Chapter I, are lint fibers and fuzz fibers, more commonly called cotton and cotton linters, respectively. The lint fibers are those removed during the ginning process. The linters have been defined[2] as "that residue of vegetable hair found on the seed of all varieties of American cotton after ginning." In their natural state, lint fibers and fuzz fibers are the purest form of cellulose found in nature. Chemically one is as satisfactory as the other. When either type is purified and bleached carefully, the purity as well as the physical and chemical homogeneity of the cellulose exceeds that obtained from any other plant fiber. Because of its value to the textile industry and the economics involved, lint fiber is not used to any extent as a source of cellulose for chemical processing. On the other hand, the use of cotton linters as a chemical raw material has developed into an extensive industry during the present century.

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[1] B. Berkman, 8th Annual Conference of Agriculture, Science, and Industry, Chicago, Mar. 25–27, 1942.

[2] G. S. Meloy, U. S. Dept. Agr., *Misc. Pub.* No. 242, Washington, May, 1936, p. 2.

Cotton linters resemble lint fibers in physical appearance only slightly. They consist of a mixture of two types of fibers: the long, usually soft or flaccid fibers that have escaped removal during ginning; and the very short, more deeply colored fuzz fibers more or less densely matted about the seed

Courtesy of Hercules Powder Co., Wilmington, Del.

FIG. 7.—CHEMICAL COTTON AND ITS SOURCE.

Cotton bolls.
Cotton seed before removing linters.
Linters before purification.
Staple cotton or lint fiber.
Cotton seed after removing linters.
Chemical cotton.

coat. The normal colors of linters are various shades of olive and light buff, although on exposure to light these may shade off to a deep buff. Weather damage, fungus staining, and other causes may develop other colors. The natural colors are easily bleached, whereas the others are quite difficult or impossible to bleach. Due to varying climatic and soil

conditions as well as to varieties of cotton planted, linters differ in maximum length and uniformity in length of the long fibers, in softness or harshness (resiliency) of the mass of fibers as a whole, and in smoothness or nappiness. The content of noncellulosic substances in linters also varies over a wide range. This variation is primarily due to the presence of dirt and field trash.

2. Development of the Cotton Linters Industry

The seed obtained as a by-product from the ginning of cotton was, until after the Civil War, used primarily for planting and to a small extent for fertilizing purposes and cattle feed. The development of this by-product into the now thriving cottonseed oil industry[3] with more than 400 mills in the United States in 1941 is a separate story. Growth of the industry in the United States was retarded, however, because most American varieties of cotton seed differed from the smooth seed varieties used in Europe in that they were covered with a heavy coating of fuzz fibers. These fibers absorbed so much oil during the pressing that the necessity for removing them soon became apparent. At that time, the seeds were not dehulled before being crushed as is the modern practice. Later the advisability of removing the fuzz in order to facilitate the handling of the seeds also became evident. The cottonseed oil industry, in itself a by-product industry, thus led to the availability of another by-product, cotton linters.

The first cotton linters produced were wasted due to the lack of a market, but their value as a stuffing material for mattresses, comforts, cushions, and upholstery soon became apparent and offered a substantial outlet for this by-product. However, there were still large quantities available for new uses.

The chemist became interested in cotton linters when cellulose became important as a chemical raw material for the nitrocellulose industry. Early in the present century, cellulose in the form of linen rags, tissue paper, and bleached cotton roving was used for the nitrocellulose industry. The high cost of these raw materials and their limited supply necessitated the search for a source of cellulose of equal purity and lower cost, and it was in cotton linters that the chemist found these requirements.

Need for tremendous quantities of smokeless powder for World War I accelerated the use of cotton linters in the chemical industry. When the United States entered the war, rules were issued governing the cutting of cotton linters and the entire crop was requisitioned for war uses. Cotton

[3] H. B. Brown, *Cotton*. McGraw-Hill, New York, 1927, pp. 432–3.

linters production rose from approximately 400,000 bales in 1910 to a high of 1,300,000 in 1916 and continued at the million-bale level until cessation of hostilities, when the market for nitrocellulose explosives collapsed. Enormous quantities of linters of varying quality and little peacetime value were then available.

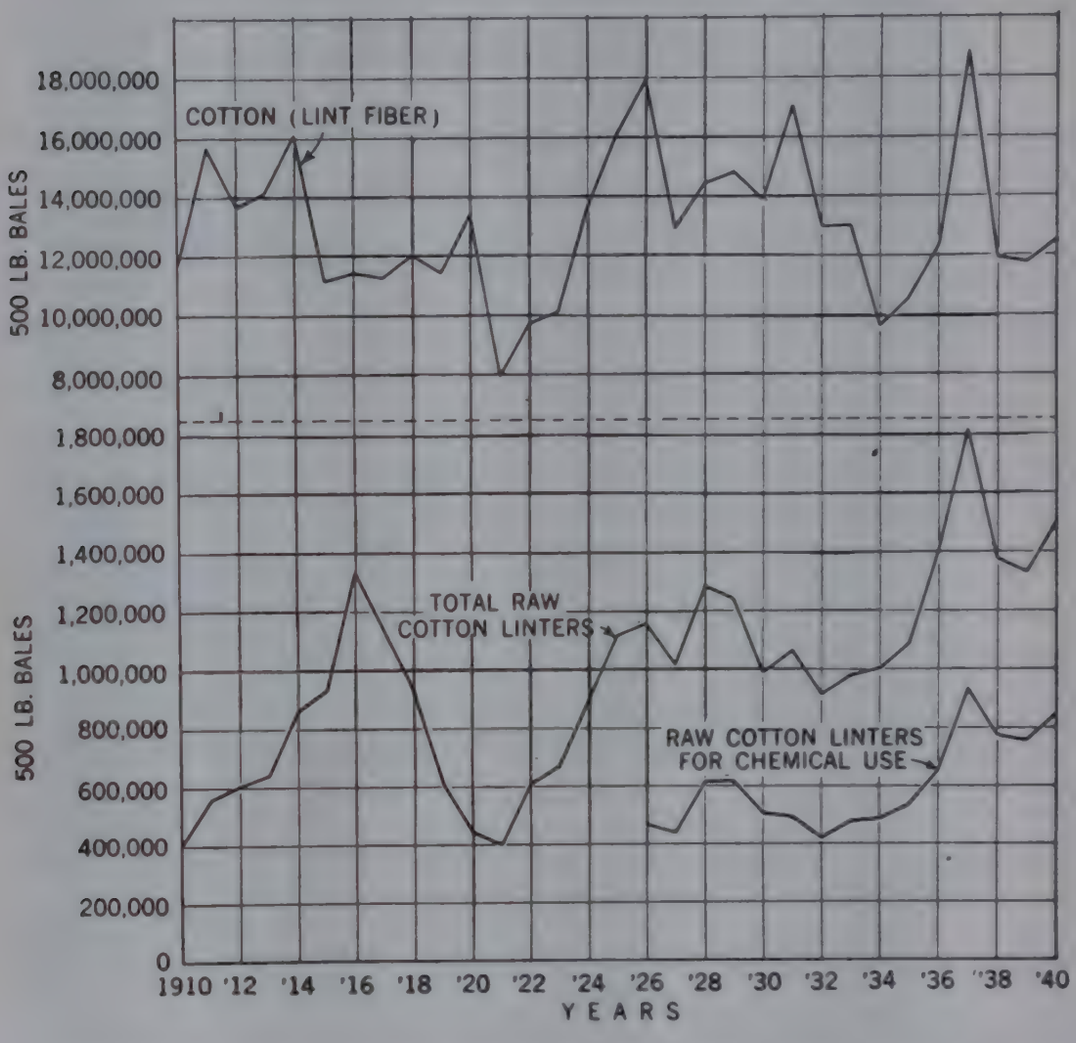

FIG. 8.—UNITED STATES PRODUCTION OF COTTON (LINT FIBER), TOTAL RAW COTTON LINTERS, AND RAW LINTERS FOR CHEMICAL USE.

Graphs prepared from data taken from U. S. Dept. of Commerce publications and from calculations made by Paul J. Weber, economic statistician, Hercules Powder Company.

Following the war, new industries calling for cellulose as a raw material advanced rapidly. Among them were rayon, lacquers, plastics, coated textiles, and commercial explosives. Because of their high purity and low cost, purified cotton linters soon were used in increasing quantities in these fields. In recent years, one of the major uses for cotton linters has

been for the manufacture of cellulose acetate. From 1937 through 1940, the chemical industry has consumed 50 to 60% of the cotton linters production in the United States. The total cotton and cotton linters production from 1910 through 1941 and the approximate linters production for chemical use from 1926 through 1941 are given in Figure 8. A comparison of cotton linters consumed in the chemical industries in 1929 and 1941 is shown in Figure 9. At the present time, cotton linters are recovered be-

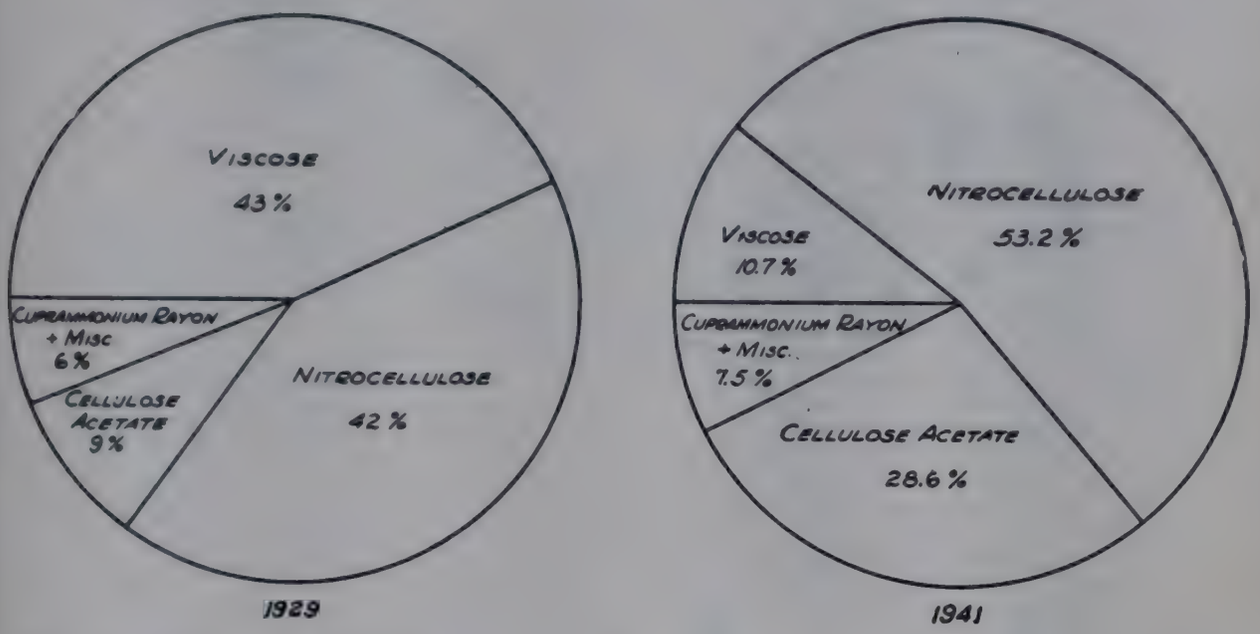

FIG. 9.—ESTIMATED CONSUMPTION OF CHEMICAL COTTON BY INDUSTRIES IN THE UNITED STATES, 1929 (MUNSON[4]) AND 1941.

cause of their economic value and eminent suitability for chemical cellulose. Due to the present war, the supply of linters is insufficient to meet the demands.

3. Delinting of Cotton Seed

Early attempts at the removal of the fiber from the seed were made primarily to improve yields of cottonseed oil with little thought given to the usefulness of the fiber removed. About sixty years ago, a machine similar in design to the cotton gin was employed for this separation. The subsequent development of this machine, differing little in basic design from the original, was gradual and was allied with the uses developed for the by-product fiber. The machine was named the "linter" machine and the process, the "delinting" operation. Soon the fuzz fibers were universally called "cotton linters."

[4] W. D. Munson, *Ind. Eng. Chem.*, **22**, 467 (1930).

In the linters room of a modern cottonseed oil mill, the cotton seeds are thoroughly cleaned on suitable screening equipment to remove field trash such as sand, clay, leaves, and pieces of cotton stalk and cotton boll. The removal of these contaminants at this stage of the process is of primary importance in the production of linters of superior quality, because once these

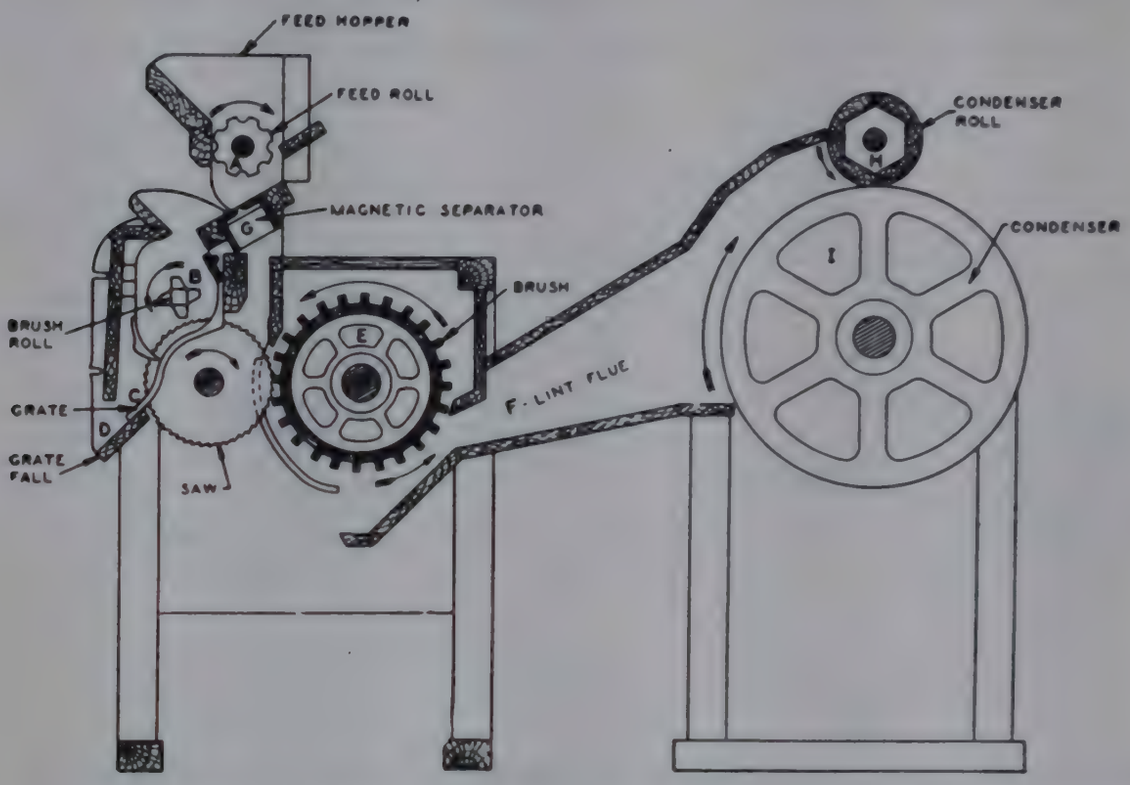

FIG. 10.—DIAGRAMMATIC SECTION THROUGH DELINTER (WOOLRICH AND CARPENTER[5]).

A. Seed feeder roll controlled by density regulator.
B. Revolving float for rolling seeds to the saws.
C. Grate through which seeds cannot pass.
D. Grate fall for delinted seeds.
E. Revolving brush for removing linters from grate and blowing them up the flue.
F. Lint flue.
G. Magnetic plate for removal of iron.
H. Condenser roll.
I. Open condenser for collecting linters.

contaminants are broken up and mixed with the linters, it is extremely difficult to remove them. The cleaned seeds are then fed into a linter machine (Fig. 10) where a first cut of linters is removed. The first-cut linters are usually collected on a rotating condenser and then baled. The seeds are now passed through a second-cut linter machine from which the linters are conveyed in an air stream to screening equipment designed to

[5] W. R. Woolrich and E. L. Carpenter, *Mechanical Processing of Cottonseed*. Eng. Expt. Sta., Univ. of Tennessee, Knoxville, 1935, p. 51.

remove tiny particles of hull bran and hull which had been scraped off the seeds by the saws. After this mechanical purification treatment, the second-cut linters are baled for shipment. In some mills, the entire removal of linters is made in one pass through the linter machine; the product is known as mill-run linters.

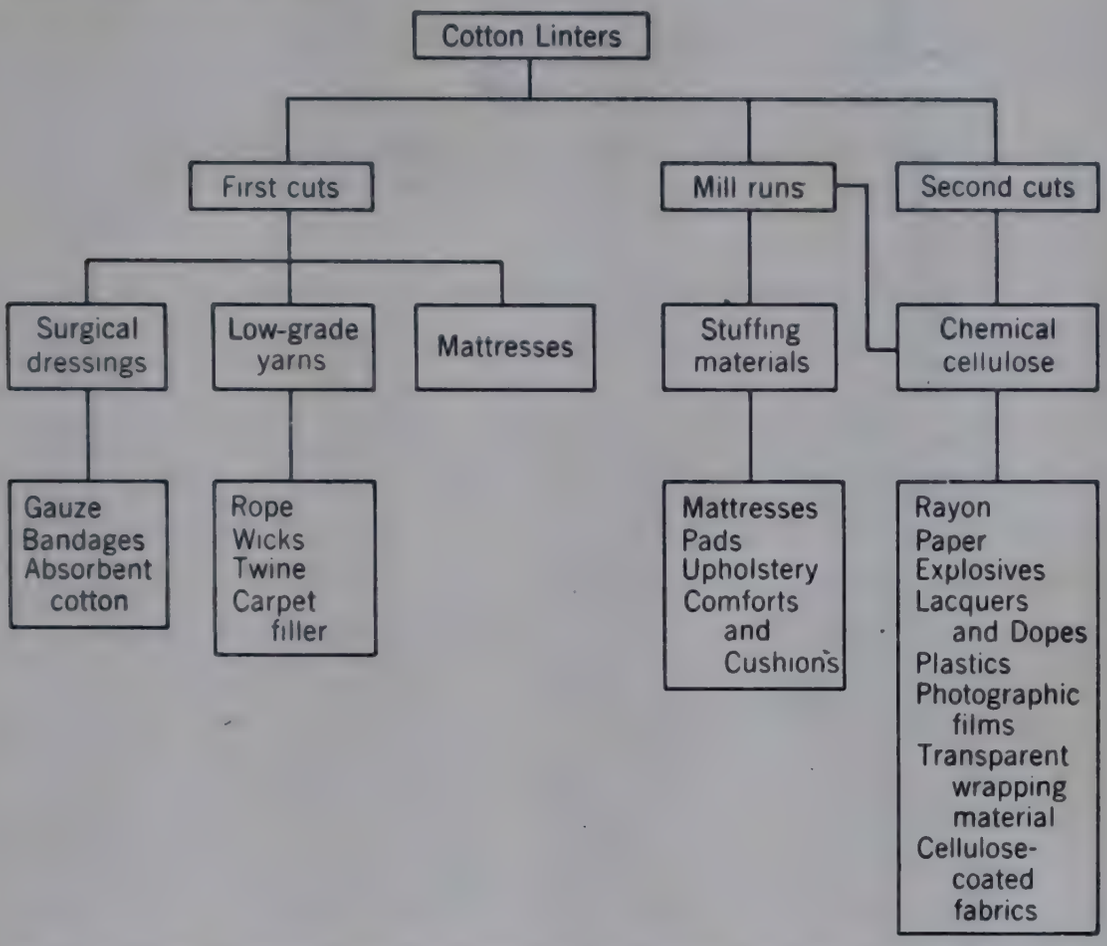

FIG. 11.—PEACETIME UTILIZATION BY INDUSTRY OF THE THREE GRADES OF COTTON LINTERS (BIEBER[6]).

The entire 1942–43 crop of cotton linters has been requisitioned by the U. S. Government for conversion to chemical cellulose.

As the result of efforts to produce cotton linters of increasingly higher quality, it was soon recognized that linters quality was affected by many factors including: the climatic conditions during growth and harvesting of the cotton, the conditions of cottonseed storage, the cleanliness of the seed, and the condition and speed of the linter machine saws.

4. Types and Grades of Linters

As indicated above, there are three general types or grades of cotton linters; namely, first cuts, second cuts, and mill runs. First cuts usually

[6] G. D. Bieber, *Chem. & Met. Eng.*, **48**, 93 (1941).

range from 20 to 75 lbs. per ton of seed and, because of their long staple length, command a premium in price. Second cuts usually range from about 100 to as high as 200 lbs. per ton of seed. These linters are about $^1/_8$ to $^1/_4$ inch in length and, because of their shortness and color, are of little use for anything but the chemical trade where their staple length is not detrimental. Mill runs usually range from about 70 to 200 lbs. per ton of seed, depending upon the market. The better grades of mill-run linters command a premium price approaching first cuts, but some of the lower grades are classed in the price range of second cuts and are used in the chemical trade. The utilization by industry of the three grades of cotton linters is shown in Figure 11.[6]

A fourth type of cotton linters made its appearance due to the active demand for cellulose for chemical purposes. There is a small amount of fuzz still attached to the seed coat or hull when the seeds are decorticated and the kernels and hulls are separated. Apparatus for grinding these hulls and separating the fibers from the bran has been installed in some mills and the fiber thus obtained is called "hull fiber." This type of cotton linters, properly prepared, is chemically as pure a form of cellulose as the other types of cotton linters. Its extremely short fiber length requires special care and technique in handling, or heavy yield losses occur.

The need for standards to measure the quality of cotton linters soon became necessary because of their many varied and growing uses. The United States Department of Agriculture was able to establish a series of standards[7] for American cotton linters which have been available since August 1, 1926,[8] and which have been generally useful to both producers and consumers.

5. Production of Chemical Cotton

Cotton linters are almost ideally adapted to the production of chemical cellulose of high alpha-cellulose content, a value of 99% being easily obtained, and of high viscosity. The usual commercial procedure[4, 9, 10] for preparing chemical cotton from raw linters consists in first removing admixed impurities by mechanical means, then digesting or cooking the linters in mild alkaline liquors, following this by a bleach operation, with inter-

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[7] U. S. Dept. Agr., Bur. Agr. Econ., *Service and Regulations Announcement* **94**, 1925.

[8] U. S. Dept. Agr., *Misc. Pub.* No. 242, p. 1; see ref. 2, p. 519.

[9] M. Steude, *Nitrocellulose*, **2**, 95 (1931).

[10] J. A. Lee, *Chem. & Met. Eng.*, **48**, 90 (1941).

mediate and final washing of the purified cellulose, and finally drying the product. A flow-sheet showing the essential steps in this process, which requires about 20 hours, has been recently published.[11] Some idea of the degree of purification which can be effected may be gained from the comparative analytical data[4] in the following table:

	Raw linters, %	Purified linters, %
Chemical yield of cellulose (by digestion with NaOH)	80–85*	...
Alpha-cellulose	...	99
Ash	1–1 5	0.10
Iron	0.06	0.002
Ether extract	1	0.20
Lignin (H_2SO_4-insoluble)	3	0.20
Moisture	6	5

* More recent data indicate yields as low as 75% for many types of linters.

Exact specifications, set up by the manufacturers of cellulose derivatives and covering the properties of chemical cotton, require that the various operations in the purification of chemical cotton be rigidly controlled. Viscosity, color, and other properties are determined to a large extent by the conditions of digestion and bleaching.

(a) *Selection of Raw Linters*

No one can successfully make chemical cotton for all cellulose derivatives unless his knowledge of the major raw material, cotton linters, is complete. Selection of raw linters is the first step in the manufacture of purified cotton linters, or chemical cotton; this selection takes place in the cottonseed oil mill and, to some extent, in the cotton fields.

Skilled workers must inspect linters physically at the mills and draw samples from individual bales (Fig. 12) representative of the lot to be bought. Each bale which passes an acceptable standard is tagged. The value of this physical inspection is proportional to the specialized knowledge of the men doing the work.

Second-cut linters are the chief source of supply for chemical cotton because they are as high in cellulose content but cheaper than the first-cut and mill-run linters, are relatively free of field trash, and are just as suitable for bleaching purposes. Cotton linters for the chemical trade are usually

[11] Anon., *Chem. & Met. Eng.*, **48**, 108 (1941).

purchased on the basis of their cellulose content as measured by laboratory purification to an unbleached pulp. The samples drawn by the field staff are either analyzed by each purchaser or by an independent laboratory using a standard testing procedure known as the "pot yield method."[12] The present basis used for price is 73% of cellulose with adjustments based on variations from this standard. This varies with the base price for linters. It is usually to the economic advantage of the oil mills, therefore, to produce the highest quality linters possible.

When the work of selection and classification of raw linters was first

Courtesy of Hercules Powder Co., Wilmington, Del.

FIG. 12.—BALE OF RAW LINTERS AS RECEIVED FROM COTTONSEED OIL MILLS.

undertaken about ten years ago, the main task was to educate the oil mills to the quality of linters needed for the chemical industry. The mills responded, new equipment was introduced, and better use made of the installed equipment, so that today not only a better quality second-cut cotton linters is produced but also a considerably greater quantity. Although the United States production in the 1940–41 season of an average of 171.1 lbs. of linters per ton of seed is the highest attained in the linters industry, the quality remained at a considerably higher level than prevailed five years ago.

The cotton season in the United States officially runs from August 1 to July 31 but the season during which oil mills operate is much shorter, in

[12] L. N. Rogers, *Oil & Soap* **14**, 199 (1937).

most cases five or six months. In order to cover the yearly requirements of the consumers of purified cotton linters, large quantities of raw cotton linters must be stored, usually at the linter purification plants.

(*b*) *Classification of Raw Linters before Purification*

The preliminary physical inspection at the oil mills is not sufficient for completely evaluating the quality of raw cotton linters for cellulose derivatives.

Each carload of inspected and tagged linters received at the linters purification plant is further tested and segregated for storage. Physical inspection for color, staple length, and dirt content classifies the linters in a general manner. Then the lots of raw linters are given a complete laboratory-scale purification treatment, duplicating the plant-scale purification methods. Chemical and physical analyses of the linters thus purified classify them still further for specific uses.

Because different derivatives of cellulose demand special types of purified cellulose and, also, different products of each derivative require special physical and chemical qualities in the chemical cotton used, there is no single test known suitable for measuring the quality of raw linters for chemical cotton. In many cases the final decision as to the suitability of a given lot of linters for conversion to some particular cellulose derivative is based on the laboratory-scale preparation of that derivative. The combination of all results obtained leads to the proper selection of raw cotton linters for a specific use.

(*c*) *Mechanical Treatment of Raw Linters before Purification*

Prior to the digestion step, the tightly packed bales of linters are opened in various ways. The layers of packed linters in some cases are fed directly to the digester. The preferred method is to open the bales mechanically by feeding them to a bale-opening machine—a rotating cylinder with bronze spikes (to prevent sparks) known as a "devil duster." The buff to brownish colored linters, which are now in a fluffy condition, are picked up by an air stream for transfer to the digesters. At this stage heavy contaminants can drop out, and additional mechanical cleaning of the linters can also be carried out.

(*d*) *Digestion*

The object of digestion is to accomplish the maximum solution of non-cellulosic and ligneous materials in the raw linters while leaving the product

at the desired level of viscosity. In addition to fats, waxes, and pectates[13] there are always present in raw linters varying amounts of the seed coat of the cotton seed, commonly called hull matter, and various types of field trash. The latter are particularly objectionable due to their resistance to alkaline liquors and can best be removed by proper seed cleaning at the oil mills.

In digestion, the factors which affect cellulose purification and viscosity reduction are concentration of alkaline liquors, temperature of digestion, and time of digestion. It is recognized that additions of small amounts of wetting agents present in the digestion liquor aids in the removal of the undesirable materials. Bolton[14] suggests the employment of certain sodium salts of sulfuric acid esters of a saturated aliphatic alcohol. Soaps and other detergents can be used.

In general, mild solutions of caustic soda (2.5 to 3.5% NaOH)[4] and a detergent are used in the digestion of raw linters, which is carried out in a batch system. Digesters may be of the vertical stationary type or the spherical rotating type. In either case, the caustic solutions must be accurately prepared and a uniform mixture of the cooking liquor and the linters in the digester is necessary to produce a uniformly digested product. Similarly, accurate control of time and temperature is essential. Each charge[10] consists of approximately 7000 lbs. of raw linters and the ratio of the caustic solution to cotton is 10:1. After displacing the air, the temperature is raised until a steam pressure of from 30 to 100 lbs. is reached and is held there for two to six hours, depending upon the desired viscosity of the product. Careful cooking in the absence of air results in saponification of the fats and waxes, destruction of the pectates, and partial or complete solubilization of the hull particles and other impurities.

At the completion of the treatment, the opening of a valve at the bottom of the digester enables the steam pressure to blow the contents of the digester up through a cyclone separator, which separates the steam from the stock. The latter drops into a steel wash-tank. The thorough washing of the gray to light-yellow cooked linters to remove all caustic after digestion is of great importance. One ton of linters requires about 30,000 gallons of water for the washing operation at this point.

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[13] R. L. Whistler, A. R. Martin, and M. Harris, *J. Research Natl. Bur. Standards*, **24**, 555 (1940).

[14] E. K. Bolton (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,048 775 (July 28, 1936).

(e) *Bleaching*

The digested cellulose freed of the bulk of the foreign matter still requires improvement, especially in color, and this is effected by bleaching with chlorine, hypochlorite, peroxides, permanganates, or other reagents. The solubilized color bodies are then extracted by washing with water or dilute solutions of alkali.

The factors which affect color and viscosity of bleached cellulose are temperature and duration of bleach, concentration, and *p*H. Sheldon[15] discloses the relations of these factors to the properties of the chemical cellulose.

Single- or multi-stage bleaching similar to that employed in wood pulp purification is used (see Chapter VII); however, the amount of substances to be solubilized by chlorination is much less. The degree of cellulose purity of the digested linters and the need to maintain this level of purity necessitate careful control of bleach conditions. Because of the special quality requirements of each cellulose derivative, it is impossible to standardize on one bleaching procedure for all purposes, and custom bleaching in batch operations is the standard practice.

Chlorine is the bleach reagent most frequently used. The chlorine, as in wood pulp bleaching, may be used as a liquid or a gas or in the form of sodium or calcium hypochlorite. The bleaching operation is carried out in large, well-agitated tubs constructed usually of a special alloy steel selected because of its resistance to all bleaching chemicals. Cellulose readily adsorbs metallic ions and care must be taken to avoid contamination from copper and iron because of the deleterious effect of these metals on the quality of many cellulose derivatives. Sulfuric acid is used as a souring agent and to reduce the ash content, and a treatment with oxalic acid is used to reduce the iron content of the linters. After each bleaching treatment, the product is thoroughly washed to remove the by-products of the bleaching reaction. During the bleaching operation, as in digestion, care is exercised in each step to produce a uniformly pure cellulose of the desired viscosity in cuprammonium solution.

(f) *Blending of Purified Linters*

After analysis of the bleached cellulose for viscosity and other chemical properties proves the material suitable for the particular customer for whom it was prepared, the cellulose is blended while wet in very large blending

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[15] L. M. Sheldon (to Cellulose Research Corp.), U. S. Patent 2,190,274 (Feb. 13, 1940).

units holding 10 to 15 tons of cellulose, dry weight. This is done to insure delivery to the customer of continuous lots of chemical cellulose of uniform chemical and physical properties. A further chemical analysis is made of the blended lots prior to drying.

Courtesy of Hercules Powder Co., Wilmington, Del.

FIG. 13.—WRAPPING BALES OF CHEMICAL COTTON FOR SHIPMENT.

(g) *Drying of Chemical Cotton*

Chemical cotton is dried and baled in sheet form for the viscose and paper trade, and in loose form for other uses. Careful drying is of extreme importance because chemically pure cellulose cannot be successfully used in the manufacture of cellulose derivatives unless it has the proper physical form and the desired physical reactivity.

Drying in loose form is preceded by pumping the blended linters, in a concentration of less than 0.5% cotton in water,[4] over rifflers for removal of any foreign matter, such as sand, which is heavier than linters. Rubber squeeze rolls reduce the moisture content to approximately 50% and pickers

revolving at high speed put the linters in a fluffy form free of lumps and ready for drying.

Drying is carried out in a long tunnel drier on a continuous traveling metal apron and moisture is removed by a current of carefully controlled heated air. Accurate control of temperature is maintained throughout the length of the drier by means of automatic controls and is dependent upon the ultimate use to which the chemical cotton is to be put. The grade destined for acetylation requires a lower temperature than most other grades. Thus, it is possible to custom-dry the cellulose for a particular use. After leaving the driers, the cellulose is passed over a magnetic separator for removal of any metal contaminants.

It is then baled, weighed, and stored until a complete cellulose analysis is made prior to shipment. Loose pulp bales are dried as a rule to a maximum moisture content of 7% and have an average weight of 145 lbs. per bale (Fig. 13).

Linters for viscose rayon are sheeted using standard papermaking equipment. Viscosity uniformity is of paramount importance, and the wet linters are blended in a continuous blending system which insures the customer a product of practically constant viscosity. After blending, the stock is processed in a beater, jordanned, and sheeted on a fourdrinier paper machine. Care is taken to prevent drying at temperatures damaging to the cellulose. Moisture of the sheeted stock must be accurately controlled within narrow limits. The stock is sheeted to a standard thickness of 0.040 inch and cut to the size specified by the customer. The cut sheets are baled, weighed, wrapped in kraft paper, and stored for complete cellulose analysis before shipment is made. Bales vary in size but are generally 150 and 200 lbs. net weight.

Chemical cotton has achieved an outstanding position in the preparation of those products in which high clarity, freedom from color, and high strength are of importance. Among the reasons for this is the exceptional purity of cellulose from cotton linters as distinguished from cellulose from other sources. Until recently, the manufacture of cellulose acetate has been almost entirely dependent on linters, the nitrocellulose industry largely so; viscose has been made from linters when requirements were exceptional as to strength and moisture resistance; for example, for use in sausage casings and rayon cord for tires.

C. RAGS

HARRY F. LEWIS

Cotton and linen rags have long been used as an important source of cellulose fibers for the manufacture of paper. In recent times, their importance in this country has been only as a source of paper and fiber stock. Abroad, however, various types of new cotton waste have been used, in the immediate past, as raw material for nitration. This discussion will be confined to the utilization of cellulose from rags in the United States.

In the earliest period in American history, rags represented almost the only raw material available for the manufacture of paper, and it might be said that the amount of paper produced was controlled by the amount of rags collected. Although rags were originally of prime importance as a raw material for almost all types of paper, gradually the introduction of sulfite and sulfate fibers, and, more recently, purified wood pulp, has seen one rag use after another apparently supplanted by a less expensive material. Today we find rags going only into high-grade bonds and writings where permanence and appearance are of importance, into blottings and fiberboards, and finally into the lower-grade products such as the felts used as a base for floor coverings or for impregnation for roofing papers.

Because of these changes, the amount of rag stock produced and converted into fine paper has fallen off considerably since the beginning of the twentieth century, although there has been very little change over the past ten years. During 1939, there were produced 83,897 tons of rag-content papers in the United States. In 1899, it is estimated that 100,000 tons of such papers were made.

The rags used for conversion into bleached rag stock, one of the purest forms of cellulose produced technically, may be either new rags or old rags. New rags include bleached cuttings from the textile field, such as light prints, white and fancy shirt cuttings, shoe cuttings, blue overalls, etc. The old rags are sold under a variety of classifications, being termed old whites, thirds and blues, blue overalls, etc.

Naturally, these different materials show considerable variation in

the noncellulosic impurities which must be removed in the cooking and bleaching processes; hence, there is some variation in processing required to remove these different components.

New rags may contain as sizing agents starch, certain synthetic resins, and saponifiable and nonsaponifiable fats and waxes. They may be white or dyed, and the dyes may be easily removable from the fabric or they may belong to the indanthrene class (fast dyes) and, therefore, be removed only with difficulty. Various resins may have been added to impart stiffness, freedom from wrinkling, or some special effect. Rubber and rubber derivatives are often present in knit goods, the latter to impart special properties to textiles. Old rags may contain, in addition to the above, inorganic and organic dirt. Although many of these added agents are removed during the normal processes employed in the mill, certain of them will cause trouble, and rags containing these should be avoided.

The cooking chemicals generally employed for removing these various impurities or rendering them susceptible to bleaching include lime, lime and soda ash, and caustic soda. Grimm[1] has studied the action of the different alkalies on vegetable and animal fibers and concluded that sodium carbonate in excess works well on vegetable but not on animal fibers, and that sodium hydroxide attacks vegetable fibers, destroys animal fibers, and saponifies waxes, fats, oils, etc.; in contrast, the use of lime results in less degradation of vegetable fibers and at the same time destroys animal fibers and colors. In general, the effect of lime on cellulose is milder than that of an analogous amount of caustic soda; hence, with stocks where the minimizing of degradation is an important factor, lime is used; in this case, the cooking period must be extended. The majority of the impurities present go into solution as soluble salts of fatty acids following saponification. Nonsaponifiable hydrocarbons are first emulsified and then may recoagulate on the fibers in the beater to appear in the finished paper.

In the presence of vat dyes of the type of indigo and the indanthrenes, the action of the cooking agent may be extended by the use of reducing agents, such as sodium hydrosulfite ($Na_2S_2O_4$) or the modified hydrosulfites, or milder reducing agents of the type of the modified starches and simple carbohydrates. Thorough mixing of the hydrosulfite with the rags in the presence of the least possible amount of air, followed by a washing operation to remove the reduced dye, is essential to good stripping of such pigments. These conditions are particularly important in the case of indanthrene-dyed rags.

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[1] H. Grimm, *Zellstoff u. Papier*, **1**, 7, 32 (1921).

Laughlin[2] has studied the effect of variables such as time, temperature, and concentration of cooking chemicals on the degradation of cellulose. He showed that a cooking process using 3.5% sodium hydroxide or 10% lime carried out for 3 hours at temperatures corresponding to 100 to 150 pounds steam would not degrade the cellulose too greatly; conditions in excess of these proved to be harmful, with pressure and chemical concentration having more effect than time.

It is almost impossible to outline any set of conditions as being standard for the processing of these various grades of rags. The amount of cooking chemical employed depends on the rag being cooked; white rags take less chemical and time than do colored ones, clean rags less than dirty ones. In the United States, the cooking operation is generally carried out in horizontal boilers having capacities running from 5000 pounds up to 16 000 pounds or more. Rarely does the caustic used exceed 10% of the weight of the rags nor the lime 20%. The rags before cooking are sorted, cut, and dusted.

The product obtained from the rag boiler after cooking and washing is generally far from the brightness desired; hence, it is necessary to remove the cooking residues by bleaching. The cooked rags are first washed, generally in a beater equipped with a washing cylinder, in order to remove soluble colored substances or loosened dirt. Lime-cooked rags are generally washed with cold water to take advantage of the greater solubility of lime in cold water. After washing is complete, the roll is lowered, and the cuttings are drawn out to separate them into threads and the threads into fibers. When this stage is achieved, bleach is added. Most rag mills employ calcium hypochlorite for the purpose, although other bleaching agents have been proposed, and one, at least, of the newer ones, sodium chlorite, is said to yield a product of satisfactory color with no degradation of cellulose.

A number of investigations have been made on the effect of the variables of bleaching on the quality of the rag stock produced. Crain[3] has considered in detail the effect of variables such as *p*H, temperature, and time of bleaching on the chemical constants and physical properties of the bleached pulp. Crain has shown that, for hypochlorite bleaches between *p*H 4.85 and 9.5, the maximum degradation as measured by viscosity occurs at or near the neutral point. Degradation also occurs more rapidly with increase in temperature; this is particularly true above 45°C. Crain's work confirms the experiments made by Birtwell, Clibbens, and Ridge,[4] by Clibbens

[2] E. R. Laughlin, *Paper Trade J.*, **97**, 39 (Oct. 26, 1933).

[3] R. C. Crain, *Paper Trade J.*, **103**, 37 (Dec. 10, 1936).

[4] C. Birtwell, D. A. Clibbens, and B. P. Ridge, *J. Textile Inst.*, **16**, T13 (1925).

and Ridge,[5] and by Davidson[6] on the action of bleaching agents on cotton to be used for textile purposes.

After a satisfactory color has been achieved, the stock is dropped into a drainer with or without washing. Here it evens up in brightness and softens up somewhat, possibly due to the degradation which may occur. Inasmuch as in the manufacture of the various grades of rag papers a mixed furnish of stocks of different sources and cooking processes is used, the drainers both improve the color and at the same time provide storage facilities for the different stocks.

The physical and chemical characteristics of the drainer stock will depend upon the quality of the rag before cooking, the severity of cooking and bleaching, thoroughness of washing, and conditions existing in the drainer. The three most commonly used chemical constants to characterize rag stocks are the cuprammonium viscosity, copper number, and alpha-cellulose content. Standard methods for carrying out the determinations have been established by the Technical Association of the Pulp and Paper Industry.[7, 8, 9] Bleached stocks in a good mill will vary in cuprammonium viscosity all the way from 30–40 up to 200–400 centipoises, in copper number from 0.1 to 1.5, and in alpha-cellulose from 90 to 98%. Few rag stocks will be obtained having the optimum values in these various ranges; it is not uncommon, however, to see bleached stocks from new rags having a viscosity of 250, copper number of 0.1, and alpha-cellulose content of 97.5%. High-grade new rag stock of this quality will contain principally alpha- and beta-cellulose; rag stock from old rags may contain small amounts of gamma-cellulose.

Since one of the chief uses of rag papers is for permanent records, a review of the present state of knowledge regarding permanence may be of interest. Extensive investigations have been carried out in the laboratories of the Bureau of Standards and The Institute of Paper Chemistry in an attempt to determine what factors control the so-called "permanence" of paper.[10] Apart from the effect of acid present in sheets having too low a *p*H, the main factors controlling the life of the sheet appear to be the quality of the pulp or stock making up the sheet. Since quality may be meas-

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[5] D. A. Clibbens and B. P. Ridge, *J. Textile Inst.*, **18,** T136 (1927).

[6] G. F. Davidson, *J. Textile Inst.*, **24,** T185 (1933); **25,** T174 (1934); **29,** T195 (1938); **31,** T81 (1940).

[7] Tech. Assoc. Pulp & Paper Inst., *Standards*, **T 206 m-37** (Sept. 15, 1937).

[8] Tech. Assoc. Pulp & Paper Inst., *Standards*, **T 215 m-38** (Jan., 1938).

[9] Tech. Assoc. Pulp & Paper Inst., *Standards*, **T 203 m-40** (Jan. 15, 1940).

[10] T. D. Jarrell, J. M. Hankins, and F. P. Veitch, *Paper Trade J.*, **95,** 28 (Oct. 6, 1932).

ured by the alpha-cellulose content and copper number, it seems safe to conclude from these experiments that the higher the alpha-cellulose content and the lower the copper number of the sheet, other factors being equal, the longer will be the life of the sheet.[11, 12] When other factors are not equal, however, high cellulose quality may be rapidly lost. Thus, in spite of careful cooking and bleaching, papers stored in an atmosphere relatively high in sulfur dioxide will lose their physical characteristics rapidly.[13, 14] Likewise, well prepared papers may be used with inks containing potentially corrosive materials; this happened during World War I with many important documents.[15]

Apart from the use of rag cellulose in the fine papers, very large amounts of rags go into the manufacture of felt for later impregnation with asphalt for roofing purposes or impregnation, coating, and printing for floor coverings. The paper used is generally soft and very porous; because a free sheet is desired, the beating process is carried out as quickly as possible, which also maintains satisfactory machine operation.

Quantities of rags also find their way into the manufacture of vulcanized fiber, which operation involves the treatment of waterleaf paper, usually made from old rags, with a solution of zinc chloride or with sulfuric acid. For many types of fiber, old rags work better than new rags or wood pulp, although the latter is used to a considerable extent. The virtues of old rags may well lie in their characteristic combination of degradation and oxidation. A number of plies of the treated sheet are combined, and the laminated sheets are passed through successive baths of ever weaker zinc chloride and finally into fresh water. After drying, pressing, and calendering, the material is ready for use in electrical insulation, in the manufacture of luggage and trunk coverings, and for other related applications.

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[11] H. F. Lewis, *Paper Trade J.*, **95**, 29 (Nov. 24, 1932); **96**, 41 (May 11, 1933).

[12] R. H. Rasch and B. W. Scribner, *J. Research Natl. Bur. Standards*, **11**, 727 (1933); **23**, 405 (1939).

[13] A. E. Kimberly, *J. Research Natl. Bur. Standards*, **8**, 159 (1932); U. S. Bur. Census, Vital Statistics, *Special Reports* **3**, No. 33, 153 (1937).

[14] M. S. Kantrowitz and R. H. Simmons, *Proc. Graphic Tech. Conference*, **1936**, 3.

[15] M. E. Whalley, "Abstract of Report to League of Nations on the Permanence of Paper," *Paper Trade J.*, **97**, 32 (July 20, 1933).

D. BAST FIBERS

KYLE WARD, JR.

This section will deal primarily with the use of bast fibers for the preparation of cellulose pulps. While it is not concerned with the use of bast fibers for textiles, there is a certain similarity in the processes involved; and, since the principal fibers used for all these purposes are the same, a very brief treatment of the purification procedures in the textile industry will also be given.

The bast fibers form fiber bundles between the outer bark and the woody portion of the stems of plants. Before they can be used in the textile industry, the paper industry, or the chemical cellulose industry, they must be separated from the wood of the stem and to a greater or less extent from the gums and other materials which hold them together to form the inner bark. The ultimate fibers of which these bundles are composed are generally short, so that, except for chemical conversion, the bundles themselves are not broken down this far.

1. Principal Bast Fibers

The principal bast fibers are flax, hemp, jute, and ramie. Others less important include sunn, kenaf, cadillo, paper mulberry, baobab, nettle, hops, and willow. Abaca, sisal, phormium, henequen, etc., are fibrovascular bundles rather than bast fibers (see Section E of this chapter).

2. Purification Procedures in the Textile Industry

The flax which is grown for fiber goes mainly into the textile field. For this purpose, the chief purification step consists of separating the bast fiber from the woody parts of the stem.[1, 2, 3] This is generally accomplished by retting and subsequent mechanical separation. The flax plant is usually pulled up by the roots and dried, the seeds are removed with rollers or with a comb, a process known as rippling, and the stalks are then sub-

[1] W. H. Gibson, *J. Textile Inst.*, **27**, P298 (1936).

[2] W. E. Emley, *Flax and Its Products*. Textile Foundation, Washington, 1942.

[3] J. M. Matthews, *Textile Fibers*. 4th ed., John Wiley, New York, 1924.

jected to the fermentation process known as retting. This is done either by submerging in ponds or rivers, or in vats where the temperature of the water can be controlled. "Dew retting", *i. e.*, spreading the straw out in the open and exposing it to the action of the dew and the sun, is also used. There are also methods of retting with pure cultures of bacteria, as well as various chemical and enzymatic methods.[4, 5, 6, 7] Prominent among the chemical retting methods are the "cottonizing" processes, usually strong alkaline treatments. These treatments break the fibers down, in some cases as far as the ultimate fibers. The resulting material may be processed on cotton machinery and has been used extensively in Europe. "Cottonizing" produces fiber of high cellulose content, and the treatments used are very similar to those used for preparing cellulose from flax. Cottonized flax and hemp, in fact, have been suggested as promising raw materials for rayon and special papers.[5]

Flax is grown in the Temperate Zones all over the world. Most of the flax grown in the United States, however, is grown for linseed oil and not for fiber. The straw from seed-flax has also had commercial application for upholstery tow and insulating quilts.[8] Seed-flax straw has also been shown to be a suitable raw material for the "cottonizing" process.

For textile purposes, hemp undergoes the same type of retting processes employed for flax.[5] The fiber so obtained is used in ropes and cordage and as a substitute for flax in the cheaper linens. Hemp is grown widely in Europe and Asia, and to a lesser extent in the United States. In the last country, its growth is controlled by law, since the narcotic, marihuana, is produced from the same plant. Efforts are being made to increase its growth, due to its importance as a fiber material.

Jute is also retted, usually in pools of stagnant water. When retting is complete (from 10 to 20 days), the bast fiber is easily separated from the woody stem. As a textile it is used in twines and cordage and in rough fabrics, such as carpet backing or burlap bags.[3, 9] India produces practically the entire world supply of jute.[10]

Ramie finds much less commercial utilization than the three preceding

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[4] C. S. Hollander and P. H. Del Plaine (to Röhm and Haas Co.), U. S. Patent 1,842,024 (Jan. 19, 1932).

[5] P. Waentig, *Z. angew. Chem.*, **39**, 1237 (1926).

[6] C. F. Goldthwait, *Textile World*, **67**, 1825, 2103 (1925).

[7] H. Bunger, J. L. Taylor, and C. A. Jones, *Am. Dyestuff Reptr.*, **30**, P673 (1941).

[8] E. C. Dryden, S. I. Aronovsky, and T. D. Jarrell, *Paper Ind. Paper World*, **21**, 972 (1939).

[9] S. G. Barker, *J. Textile Inst.*, **31**, P12 (1940).

[10] N. C. Chaudhury, *Jute and Substitutes*. 3rd ed., W. Newman & Co., Calcutta, 1933.

fibers. The reason for this lies, in part at least, in the difficulty of purifying and spinning the fiber. Simple retting is not sufficient for removing the bast fiber, as in the case of the preceding crops, and none of the many mechanical methods suggested for decortication has established itself industrially. In China, the bast fibers are stripped off by hand in long ribbons. The bark and some of the gums are scraped off, also by hand. The fiber so obtained must be further degummed before spinning, which is difficult to do without injury to the fiber. Retting is not satisfactory and chemical treatments, especially alkaline cooks, seem to be the most promising. Ramie is grown in quantity only in the Far East,[11, 12] although small plantings, mostly for experimental purposes, have been made at many places in the southern part of the United States.

Sunn is prepared by a retting process similar to that used for true hemp and finds its main use in the preparation of nets and cordage.[10] This plant is grown extensively in Southern Asia.

Kenaf is used like jute for cordage and sacking, but is, in general, inferior.[3, 10] Cultivation and processing are also similar to that of jute. Kenaf is said to have been introduced into India from Africa,[10] but the commercial crop is almost entirely obtained from India today. In fact, one name for the fiber is Deccan hemp. Gambo hemp and ambari hemp are other names for the same material.

Cadillo or urena fiber[3] is the bast fiber from certain tropical shrubs which include *Urena lobata* and *Urena sinuata*. These fibers, with those from some other shrubs, are now being designated as Cuban jute and are recommended as substitutes for true jute.[13]

The bast fiber of the paper mulberry is unusual in that the fiber is processed into a fabric without either spinning or weaving. The clean fibers are laid out wet in several layers and allowed to dry overnight. The next morning they will be found to have adhered to each other to form a single layer which is beaten with a wooden mallet until it forms a smooth strong cloth.[3] The paper mulberry is grown in India and Japan and on the islands of the Pacific.

The bast fiber of the baobab, or monkey's bread tree (*Adansonia digitata*), is known as Adansonia fiber and finds some use as cordage.[14] The tree is a native of Africa, but is now grown in both the East and the West Indies.

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[11] J. W. Brown, *Textile Colorist*, **63**, 532 (1941).

[12] G. L. Carter and P. M. Horton, *Ramie*. Louisiana State Univ. Studies No. **26**, L. S. U. Press, Baton Rouge, 1936.

[13] C. F. Wicker, *Cord Age*, **37**, No. 2, 16 (1942).

[14] K. Braun, *Faserforschung*, **8**, 90 (1930).

The nettle is reported to be an excellent textile fiber and received a great deal of attention in Germany during the war years of 1914–1918. The fiber content of the wild nettle is about 6%, but this was increased by cultivation to 12–13%.[15] The fiber may be separated from the stalk by retting, as with flax, or by mechanical decortication, as with ramie. In either case, strips of fiber are obtained which must be chemically degummed.[3] Pulping the whole stalk, with subsequent separation of the long bast fiber and the shorter woody fibers, has also been recommended. The difficulty of obtaining a sufficient amount of fiber cheaply enough has apparently prevented the extended use of this fiber.[16]

The hop fiber can be separated by retting,[17] but the process is time-consuming and not very practicable.[15] Chemical methods[18] have also been tried, but, except in Europe from 1914 to 1918, aroused little interest. Now, in another period of war, Germany is again investigating its use in textiles.[19]

The bast fiber of the potato plant has been studied in Germany for textile purposes, but it does not appear to be economically practicable[20] under normal circumstances.

The bast fibers of certain trees, such as the willow[21] or sequoia[22, 23] have found some very limited applications in textiles, usually as cordage or felting materials. The bast of the castor bean plant[24] has also been recommended for this purpose.

3. Cellulose Pulps from Bast Fibers

The bast fibers have never had any industrial importance in the preparation of rayon or of chemical cellulose, except where the present increased demand and interrupted commerce in cotton and wood pulp may have caused a recent development of the industry. However, there is considerable patent literature on the subject. The following is a brief summary of the methods proposed for the utilization of these materials.

It will be readily seen that there are three possibilities to be evaluated

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[15] M. Lüdtke, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 65 (1938).
[16] O. Routala and J. Sevón, *Cellulosechem.*, **8**, 16 (1927).
[17] D. N. Honn, U. S. Patent 1,060,255 (Apr. 29, 1913).
[18] O. Reinke, *Chem.-Ztg.*, **39**, 597 (1915).
[19] J. Löbering, *Melliand Textilber.*, **22**, 235 (1941).
[20] M. Lüdtke, *Cellulosechem.*, **18**, 5 (1940).
[21] W. Steite, *Faserforschung*, **14**, 65 (1939).
[22] J. M. Leaver (to Pacific Lumber Co.), U. S. Patent 1,659,033 (Feb. 14, 1928).
[23] Anon., *Textile Research*, **12**, 26 (1942).
[24] W. W. Floyd, *Southern Pulp Paper J.*, **3**, No. 2, 7 (1940).

if any bast fiber plant is considered as a source of cellulose. First, the separated bast fiber may be used. However, the quality of these long fibers is very high, and they are usually too valuable for textile purposes to compete with chemical cotton or wood pulp in the cellulose industry, except in the form of rags or similar textile wastes. Second, the woody residues from the bast fiber separation may be pulped. These residues have received considerable attention in the case of the important textile materials, flax and hemp. Third, the entire stem may be treated. This is not simple, for a process capable of completely pulping the woody portion is liable to be too strong for the bast fibers, which usually require a much less severe treatment. All three types of material from the more common bast fiber plants have been suggested from time to time as potential sources of cellulose.

Linen rags and textile wastes are used for paper rather than the original fiber, although flax stems are used for paper in France and Italy, and its growth as a source of rayon and chemical pulp has been discussed as a possibility.[1, 25] Most of the processes suggested for pulping flax are alkaline processes. Pulping scutched flax straw with sodium hydroxide (greater than 8%)[26] has been reported to give a product suitable for nitration or rayon manufacture. The use of air and steam in conjunction with alkali is reported to separate the flax stalk into textile fiber from the bast and cellulose (for paper or rayon) from the shive.[27] The use of sodium carbonate or potassium hydroxide for either fiber-flax or seed-flax straw followed by bleaching treatments has also been recommended for this purpose.[28, 29] The use of a mixture of caustic soda and sulfur in the cooking liquor for the preparation of paper pulp from flax tow has also been patented.[30, 31] Another type of alkali cook recommended contains mainly trisodium phosphate in the presence of smaller amounts of an aluminum salt,[32] while still another uses lime.[33] Various other processes have been

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[25] E. Rubens, *Nitrocellulose*, **5**, 3, 19, 42 (1934).

[26] G. A. Lowry and J. A. Grant (to M. H. Ittner), U. S. Patent 2,064,929 (Dec. 22, 1936).

[27] H. Plant (to N. V. Exploitatie Maatschaapij voor Chem. Uitv. (E.C.U.)), U. S. Patent 2,243,050 (May 20, 1941).

[28] C. Ruzicka and C. V. Sale, Brit. Patent 502,451 (Mar. 17, 1939).

[29] C. Ruzicka and C. V. and G. S. Sale (trading as Sale & Co.), Brit. Patent 501,485 (Feb. 28, 1939).

[30] E. P. Jones (to Champagne Paper Co.), U. S. Patent 2,099,400 (Nov. 16, 1937).

[31] E. P. Jones (to Champagne Paper Co.), U. S. Patent 2,161,763 (June 6, 1939).

[32] F. R. Chesley, Jr., U. S. Patent 2,073,682 (Mar. 16, 1937).

[33] F. Frisch, German Patent 612,730 (Apr. 11, 1935).

suggested, including chlorination,[34, 35, 36] sulfurous acid treatments,[37] sodium sulfite cook followed by boiling with soap solution,[38] and digestion with mixtures of sodium bisulfite, sodium sulfite, and small amounts of neutral salts.[39] The separation of cellulosic fibers by means of the so-called "horn angle" machine has also been patented,[40] with a long list of fibers, including flax, listed in the specifications. Essentially, this machine is a press consisting of rotating cylinders internally tangent to each other. An auxiliary pulping step is mentioned as desirable in some cases. Flax shives, which are usually burned, are suitable[19, 41] as a raw material for wallboard or cellulose. Pulping tests on this material have shown that the sulfite process is unsatisfactory,[42] that the alkali process requires a high temperature and long cook,[43] and that a modified sulfate cook (sodium hydroxide, sodium sulfide, and sodium carbonate) gives an extremely short-fibered cellulose which would have limited applicability in the paper industry and which is economically unpromising for rayon or chemical conversion, since the requisite purification gave low yields.[42] A similar modification, on the other hand (sodium hydroxide and sodium sulfide), has been patented as particularly suitable for producing rayon pulp.[44] It has been reported that the nitric acid pulping process yields a pulp suitable for the preparation of viscose,[45] and such processes have been recommended for producing high-grade paper pulps from flax tow, flax straw,[46] and flax chaff.[47] The Forest Products Laboratory has made

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[34] U. Pomilio, Brit. Patent 480,170 (Feb. 15, 1938).

[35] U. Pomilio, Brit. Patent 489,302 (July 25, 1938).

[36] V. I. Minaev and S. S. Frolov, *Trans. Mendeleev Congr. Theor. Applied Chem.*, 6th Congr., **2**, Part 1, 792 (1935); *Chem. Abstracts*, **30**, 4004 (1936).

[37] R. B. Wolf, R. P. Hill, and R. S. Hatch (to Lignocellulose Corp.), U. S. Patent 1,804,967 (May 12, 1931).

[38] G. R. Bencraft (to Meigs, Bassett & Slaughter), U. S. Patent 2,054,779 (Sept. 15, 1936).

[39] H. Wenzl, U. S. Patent 1,611,969 (Dec. 28, 1926).

[40] M. J. Stacom, Brit. Patent 492,524 (Sept. 16, 1938).

[41] M. Lüdtke, *Melliand Textilber.*, **20**, 253 (1939).

[42] G. Jayme, H. Pfretzschner, and J. Ditz, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 46 (1938).

[43] E. Wedekind, H. Grasshof, and O. Müller, *Papier-Fabr.*, **35**, Tech.-wiss. Tl., 513 (1937).

[44] B. Porrino, I. Mutti, and I. Fazzioli, Brit. Patent 496,015 (Nov. 23, 1938).

[45] P. Eckert and K. Plaeschke, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 113, 129 (1938).

[46] R. E. Rindfusz and V. Voorhees, U. S. Patent 1,430,115 (Sept. 26, 1922).

[47] V. Schweikart, Brit. Patent 538,222 (June 19, 1939); *Brit. Chem. Abstracts*, **1941**, B, II, 341.

an extended study of the pulping of seed-flax straw,[48] using lime, caustic soda,[49] various modifications of the kraft process, sulfite,[50] caustic soda and sulfur, chlorine,[51, 52] and some less important processes. Satisfactory paper pulps were produced, but it was concluded that except at high price levels for pulpwood, flax straw could not compete in low-cost papers. However, the situation is different for special thin papers, and flax straw has been used for the production of bast fiber as a substitute for linen rags in the manufacture of bank note, currency, cigaret, and condenser papers.[53] The flax straw is decorticated by breaking between rolls to "fine tow" amounting to about 20% of the straw. It is then cooked with approximately 15% caustic soda and 5% sodium sulfide. The ultimate yield of paper is one ton for fifteen tons of straw. It was estimated that approximately 200,000 tons of seed-flax straw would be used in the United States in 1942 for the manufacture of cigaret paper.[54]

Hemp fiber is very similar to flax fiber and finds similar utilization in special papers and board,[55, 56, 57] especially in conjunction with linen rags or flax fiber. Since hemp can be grown with a high yield per acre, its cultivation purely as a source of cellulose has been suggested.[58] As with most of the bast fibers, the problem is economic, as the cellulose produced compares favorably with cotton cellulose. It has, in fact, been reported that chlorine-treated hemp yields a more stable nitrate than cotton does.[59, 60] It is one of the fibers suggested for use with the Pomilio chlorination method.[51] Other suggested processing methods include pulping

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[48] E. R. Schafer and C. E. Curran, U. S. Forest Products Laboratory, Mimeographed Report **R1159** (1938).

[49] C. C. Heritage, E. R. Schafer, and L. A. Carpenter, U. S. Patent 1,922,366 (Aug. 15, 1933).

[50] L. Bradley and E. P. McKeefe, Canadian Patent 265,500 (Nov. 2, 1926).

[51] U. Pomilio, *Ind. Eng. Chem.*, **31**, 657 (1939).

[52] R. H. McKee, U. S. Patent 1,932,904 (Oct. 31, 1933).

[53] C. G. Worthington and C. A. Jones, *Southern Pulp Paper J.*, **2**, No. 8, 12 (1940).

[54] E. C. Lathrop and J. H. Shollenberger, Tech. Assoc. Pulp & Paper Ind., Feb. meeting, 1942.

[55] P. Kokin and E. Fridman, *L'no-Pen'ko-Dzhutovaya Prom.*, **8**, No. 5, 12 (1938); *Chem. Abstracts*, **34**, 6448 (1940).

[56] *Manufacture of Pulp and Paper.* Vol. IV, McGraw-Hill, New York, 1938.

[57] J. L. Merrill, U. S. Dept. Agr., *Bull.* **322** (1916).

[58] E. R. Schafer and F. A. Simmonds, *Ind. Eng. Chem.*, **21**, 1241 (1929).

[59] N. Parravano and G. Centola, *Gazz. chim. ital.*, **66**, 735 (1936); *Chem. Abstracts*, **31**, 3292 (1937).

[60] M. Tonegutti and E. Brandimarte, *Ann. chim. applicata*, **29**, 350 (1939); *Chem. Abstracts*, **34**, 620 (1940).

with neutral sulfite solutions,[61] with sulfite-bisulfite mixtures,[38] and with various alkaline liquors, such as caustic soda and sulfur,[30, 31] or caustic soda and sodium sulfide.[44] One series of patents describes the use of nitric acid pulping with hemp to produce cellulose pulps suitable for various purposes, including regenerated sheets and esterification.[62, 63, 64] The production of hemp pulps high in alpha-cellulose has been claimed, using a preliminary treatment with sulfur dioxide, followed by a bisulfite digestion and an alkali cook.[65] Pulps suitable for rayon production are also said to be produced if an alkaline cook (sodium carbonate or potassium hydroxide) is followed by bleaching.[28, 29] The rayon pulp derived from hemp fibers by pulping with a mixture of sodium hydroxide, sodium silicate, and a sulfonated oil refers specifically to Manila hemp, which is not a bast fiber.[66] Under the proper conditions, treatment with caustic soda alone is recommended for producing high alpha-cellulose pulps.[67] In the presence of air and steam, a caustic soda cook is reported to separate the stalk into textile fiber from the bast and paper or rayon cellulose from the hurds.[27] Hemp is also one of the fibers listed in connection with the "horn angle" rolls.[40] Another patent, covering mechanical separation of bast fiber from woody stem and mentioning hemp as one of the suitable fibers, suggests the use of either bast or wood for paper and the use of bast fiber after further purification for dissolving pulp.[68] Hemp hurds correspond to flax shives as a waste product of the textile industry. Hurds, chaff, and other wastes of the hemp industry have been shown to be raw materials for cellulose and paper pulp,[19, 69, 70] and are being used in Italy for rayon pulp.[41] The purification processes by which satisfactory pulps and papers are reported to have been obtained are generally alkaline:[71]

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[61] P. Rossignoli, *Ind. carta*, **5**, 451 (1938); *Chem. Abstracts*, **33**, 4017 (1939).

[62] A. Hoche, U. S. Patent 2,058,791 (Oct. 27, 1936).

[63] A. Hoche (to Cellulose Research Corp.), U. S. Patent 2,076,817 (Apr. 13, 1937).

[64] A. Hoche (to Cellulose Research Corp.), U. S. Patent 2,095,194 (Oct. 5, 1937).

[65] G. A. Richter (to Brown Co.), U. S. Patent 1,841,551 (Jan. 19, 1932).

[66] E. C. Worden (to Hanson and Orth), U. S. Patent 1,899,223 (Feb. 28, 1933).

[67] G. A. Richter (to Brown Co.), U. S. Patent 1,945,202 (Jan. 30, 1934).

[68] C. R. Faulkender (to Milkweed Products Development Corp.), U. S. Patent 2,240,-113 (Apr. 29, 1941).

[69] T. K. Bel'skiĭ, *Bumazhnaya Prom.*, **14**, No. 5, 65 (1935); *Chem. Abstracts*, **29**, 7071 (1935).

[70] W. Bratkowski, *Ann. acad. sci. tech. Varsovie*, **2**, 71 (1935); *Chem. Zentr.*, **1938**, II, 2671; *Chem. Abstracts*, **34**, 6082 (1940).

[71] M. J. Connolly, U. S. Patent 2,080,533 (May 18, 1937).

lime,[33] lime followed by a sulfate cook,[72] caustic soda alone,[42, 73] or in the presence of lime or sodium sulfide.[74] The soda cook produces a short-fibered weak pulp which may be admixed with sulfite pulp for the manufacture of standard book and magazine papers. The features governing its use are location and dependability of supply rather than any lack of suitability for the purpose mentioned.

Studies aimed at producing cellulose pulps from bast fibers usually deal primarily with flax or hemp, while the other fibers generally find mention in the literature only as further examples to which the method may be applicable. Processes for preparing cellulose from jute, therefore, will in general be recognized as those already mentioned. However, at least some investigators who have studied jute specifically believe it may be utilized for cellulose and paper pulp, if necessary.[25, 75] Jute wastes, jute butts (the butt ends of the stalks), and jute rags are used in the paper industry, but the digestions with lime usually employed in pulping are not intended to effect complete removal of lignin.[10, 33, 56, 76, 77] Other processes which have been suggested for pulping jute include alkaline digestion (caustic soda,[26, 27, 67] caustic potash,[29] sodium carbonate,[28] or trisodium phosphate liquors[32]) and various sulfite cooks (free sulfur dioxide,[37] mixtures of sulfite and bisulfite,[39] and mixtures of sulfite with the sodium salt of a weak acid[78]). Jute is another of the fibers for which the application of "horn angle" pressures has been suggested.[40] A rather unusual method suggested for jute and other fibers consists of retting the stalk with the sap of the banana plant.[79]

The processes of decortication and degumming by which ramie fibers are purified for textile purposes are much too costly for use in preparing industrial cellulose pulps and, although experimentation with this fiber is under way, it has received less attention than the preceding fibers. Besides the mechanical action of the "horn angle" rollers,[40] several pulping

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[72] B. Millov and E. Soldatova, *Bumazhnaya Prom.*, **12**, No. 9, 25 (1933); *Chem. Abstracts*, **28**, 4227 (1934).

[73] L. H. Dewey and J. L. Merrill, U. S. Dept. Agr., *Bull.* **404** (1916).

[74] N. V. Golub and A. I. Lur'e, *Bumazhnaya Prom.*, **14**, No. 1, 56 (1935); *Chem. Abstracts*, **29**, 4171 (1935).

[75] O. Heigis, *Chem.-Ztg.*, **35**, 1346 (1911).

[76] E. Sutermeister, *Chemistry of Pulp and Papermaking*. 3rd ed., John Wiley, New York, 1941.

[77] J. Traquair, *Paper Trade J.*, **94**, 34 (June 30, 1932).

[78] C. A. Braun, French Patent 638,011 (May 14, 1928); Addition 35,816 (Mar. 28, 1930).

[79] F. G. P. Leao, Brit. Patent 293,219 (July 5, 1928).

processes intended primarily for other fibers are stated in patent specifications to be suitable for ramie. These include caustic soda[26, 27, 67]; trisodiumphosphate[32]; sodium carbonate-sodium sulfide liquors, with or without sodium sulfite[80]; sodium sulfite, either preceded by a chlorine treatment[81] or followed by cooking with a soap solution[38]; and mixtures of alkali, sodium sulfide, and ammonia.[82]

In addition to the four preceding plants, several minor bast fiber plants have been suggested as sources of cellulose or paper pulp, such as sunn,[83, 84] kenaf,[85] hops,[18, 19, 86] and nettles.[87, 88] These are usually pulped with caustic soda. The latter two fibers are mentioned in the "horn angle" patent.[40] Large-scale experiments are now being made in Germany on pulp from potato tops, and satisfactory paper is reported to have been made,[89, 90, 91] but it is likely that this material is only of interest when the normal supply of raw materials has been cut off. The mechanical separation of bast fiber and woody fiber from the stems of the milkweed and the sunflower has also been recommended, with the subsequent use of both types of fiber.[68]

It has been contended that bast fibers from trees differ markedly in chemical composition from such fibers as flax, jute, ramie, etc.[92] However, the bast fibers of several trees are suitable for cellulose and paper pulp. The bark of the baobab has been used to a limited extent in papermaking for some time, usually undergoing a caustic soda pulping process.[14, 93, 94] Another tree bast is the paper mulberry, which is used

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[80] G. A. Richter (to Brown Co.), U. S. Patent 1,921,539 (Aug. 8, 1933).

[81] G. A. Richter (to Brown Co.), U. S. Patent 1,935,728 (Nov. 21, 1933).

[82] A. B. Bori and J. M. Estape (to Estape), U. S. Patent 1,920,239 (Aug. 1, 1933).

[83] Y. Nakamura and Y. Mima, *Rept. Govt. Sugar Expt. Sta. Tainan, Formosa*, **7**, 219 (1940); *Chem. Abstracts*, **35**, 5694 (1941).

[84] J. H. H. Ross, *Faserforschung*, **8**, 36 (1929).

[85] F. Heim, L. Matrod, and F. Moreau, *Bull. l'office colonial*, **12**, 247, 321 (1919); *Bull. Agr. Intelligence* (now *Intern. Rev. Agr.*), **10**, 1140 (1919).

[86] R. Schwede, *Jahresber. Ver. angew. Botan.*, **16**, 8 (1918).

[87] J. Hubner, *World's Paper Trade Rev.*, **47**, 711 (1907).

[88] G. Sellergren, *Svensk Papperstidn.*, **28**, 613 (1925); *Chem. Abstracts*, **20**, 1516 (1926).

[89] W. Schieber, *Vierjahresplan*, **4**, 695 (1940); *Chem. Abstracts*, **35**, 2717 (1941).

[90] R. Peuckert, *Vierjahresplan*, **4**, 697 (1940); *Chem. Abstracts*, **35**, 2717 (1941).

[91] P. Reinhold, *Vierjahresplan*, **4**, 699 (1940); *Chem. Abstracts*, **35**, 2717 (1941).

[92] R. S. Hilpert and W. Knackstedt, *Ber.*, **72B**, 1582 (1939).

[93] J. S. Remington, *Ind. Chemist*, **5**, 115 (1929).

[94] J. S. Remington, D. A. Bowack, T. P. Heald, and Alfred Davis, *Paper Mill*, **34**, 17 (Oct. 28, 1911).

extensively for preparing special papers in the Orient. This may be pulped either by the alkali[95] or the kraft process.[96] The bark of the ordinary mulberry [87, 96] has also been used by the paper industry. Caustic soda digestion has been recommended for this material.[97] The preparation of satisfactory rayon pulp from sequoia bark has also been described, using nitric acid pulping for this purpose.[22, 98]

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[95] S. P. Cane, H. Heather, and L. G. S. Hebbs, Brit. Patent 346,813 (April 7, 1931).

[96] A. Heiduschka and Yung-Hui Chang, *Cellulosechem.*, **17**, 77 (1936).

[97] Z. V. Uchastkina and V. Ya. Matveev, *Tsentral. Nauch.-Issledovatel. Inst. Bumazh. Prom., Materialy*, **1934**, No. 4, 100; *Chem. Abstracts*, **29**, 7072 (1935).

[98] F. Greenbaum, *Oesterr. Chem.-Ztg.*, **27**, 129 (1924).

E. STRAW, GRASSES, AND SIMILAR MATERIALS

SIDNEY D. WELLS

This section is limited to a discussion of the preparation of cellulose from cereal straws, grasses such as bamboo, bagasse, and cornstalks, and an evaluation of these materials as sources for cellulose. Flax straw and hemp wastes are discussed under bast fibers in Section D of this chapter. In addition, brief mention is made of the fibrovascular elements.

1. Cereal Straw

Rye, wheat, oat, and barley straws have been an important source for cellulose fiber since the invention of paper between 25 and 58 A.D. by Tsai L'un, secretary in the court of Honaug-Han, emperor of China. In fact, the use of straw antedated linen and cotton rags as well as wood pulp, the most important source of cellulose at the present time. At the time of and prior to about 1860, straw was the principal source for cheaper papers, and most of the newspapers of that period were manufactured from a mixture of rag and straw soda pulp. Newspaper files of the Civil War period in our large public libraries are in much better condition than those of the first World War because of the greater permanency of straw pulp as compared with groundwood pulp.

With the advent of the sulfite, soda, and sulfate processes for pulping wood (in addition to the mechanical process which was invented in 1855), the use of straw was replaced by wood pulp on account of the lower cost of producing the latter, and straw pulp is now used only in papers where it is desired to impart properties not possessed by papers made from the more recent competitors. Advances in the art of pulping, however, have greatly enlarged the possibility of reducing the cost of pulps from cereal straws. Some of the more recent processes, such as multi-stage bleaching with chlorination and caustic extraction, have so improved the quality and so enlarged the range of properties which can be obtained that it seems probable that the use of straw may attain a relatively more important role in the future. In the older and longer established industrial countries, straw has always retained its position as a source of cellulose, and it

seems reasonable to expect that it will regain it to an important extent in the United States as the supply of virgin timber becomes more limited and dependence upon second or third growth cordwood more common.

Most of the straw used for paper pulp in the United States is cooked with milk of lime, dolomite lime being preferred. About 10% of calcium oxide or 13% of burnt dolomite is required. The cooking is carried out in spherical rotary digesters at a temperature of about 115°C. for 8 to 10 hours. There is usually considerable false pressure, so that the pressure as shown by the pressure gage will usually be at least 45 pounds per square inch. After cooking, the pressure is relieved (this is accompanied by the escape of considerable ammonia produced during the digestion), and the contents are dumped upon a conveyor and piled into heaps for drainage and a further softening of the knots and more resistant portions through seasoning in the presence of the spent lyes. The material is then washed in beaters equipped with drum washers, or the spent liquor is pressed out by means of screw or roll presses, and the fibers separated by passage through rod mills. It may be further washed on vacuum filters or decker washers and is then suitable for further treatment with jordans for the manufacture of corrugated paper, capstock, egg-case filler board, and ordinary stiff cardboard.

The yield of board obtained is usually between 65 and 70% of the weight of straw used; the mineral matter present varies from 10 to 15%, of which about half is silica and the other half magnesia and/or lime.

Where the straw is reasonably free from weeds and has been baled while dry and stored under cover, the pulp obtained as described above can be bleached with chlorine, caustic extraction, and hypochlorite in several stages to produce a superior white pulp which is suitable for high-grade uses. Only since 1932 has availability of suitable equipment made this procedure possible and, then, only in locations where stream pollution from the spent cooking lyes is not objectionable. Ultimate yields up to 50% of the weight of the dry straw are obtained; this fiber is softer and not so easily slowed down in draining properties.

Among the foremost common cereals, rye straw is preferred because of its somewhat longer fiber and higher cellulose content; wheat straw comes next. Oat straw is used where the supply of the other two is inadequate; the yield of cellulose obtained therefrom is noticeably lower, and the pulps produce a paper or board inferior in strength. Barley straw is objectionable on account of the beards which are not readily reduced in the cooking operation.

The use of the soda and sulfate processes is well established in continental Europe and, since the beginning of the battle of the Atlantic, in Great

Britain. The silica present in the straw interferes with settling in the causticization of the recovered soda, so that recoveries of 65 to 80% are more common as compared with 80 to 90% for soda and kraft pulp mill practice using wood.

In recent years, several pulp and paper mills have been built in South America, South Africa, Europe, and the Philippines which use the Pomilio process for the pulping of cereal straw and bagasse. The process consists of digestion of vegetable fibrous material with caustic soda at moderate temperature and concentration, washing, treatment with chlorine gas, extraction with dilute caustic soda solution, washing, and bleaching with calcium hypochlorite. It differs from the multi-stage bleaching of mildly cooked soda pulps in that a much greater part of the pulping and purification of the plant material is accomplished by the chlorine than by the caustic soda.[1] The electrolytic production of chlorine and caustic soda is an important part of the process, and sodium chloride is considered the primary chemical rather than caustic soda and chlorine.

Caustic soda will pulp wheat and rye straw[2] if the chopped material is passed through two rod mills in series at temperatures between 95 and 98°C. in the presence of five to six times its weight of water. The pulped material can be further purified by digestion under pressure in rotary cookers at 60 pounds pressure with an excess of caustic soda.[3] The partially spent cooking liquors can be used as the source of caustic soda in the preliminary treatment with rods, so that a two-stage cooking system results with countercurrent flow of the cooking chemical. Unusually effective utilization of the chemical is thus attained, with higher yields and more effective use of equipment because of the reduction in bulk of the straw through the rod mill action.

Straw may be pulped effectively by means of sodium carbonate and sulfur,[4] or sodium carbonate and sodium sulfite.[5] Both processes have been adopted by American strawboard manufacturers in the production of superior corrugating paper under the name of "Strawkraft" and odorless egg-case fillers under the name of "Nuprocess." Yields of 65 to 70% of fiber are realized, and products are obtained which are from 50 to 100% stronger than corresponding products cooked with lime.

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[1] U. Pomilio, *Ind. Eng. Chem.*, **31**, 657 (1939).

[2] S. D. Wells and P. A. Forni, *Paper Trade J.*, **112**, 32 (June 12, 1941).

[3] S. D. Wells, U. S. Patent 2,029,973 (Feb. 4, 1936).

[4] S. D. Wells, U. S. Patent 1,626,171 (Apr. 26, 1927).

[5] J. D. Rue, S. D. Wells, and F. J. Rawling, U. S. Patent 1,724,778 (Aug. 13, 1929); J. D. Rue and W. Monsson, *Paper Trade J.*, **81**, 52 (Oct. 8, 1925); 49 (Nov. 12, 1925).

2. Bamboo

Bamboo is now an important source of cellulose in Burma. The process used is the soda process as modified by Raitt[6]; it involves the preliminary crushing of the bamboo nodes and countercurrent use of the alkali in a two-stage digestion. Higher yields of cellulose are obtained than from cereal straws, but the operation must bear the cost of the collection, whereas with cereal straw this cost is borne by the grain. In Burma, where the supply of bamboo is enormous and labor exceedingly cheap, an industry of considerable magnitude has become established.

3. Bagasse and Cornstalks

Bagasse and cornstalks have been the subject of papermaking developments on numerous occasions during the past ninety years. They have all failed because of the bulkiness of the material, the large proportion of nonfibrous less-resistant cellulose in their structure, and the fact that most attempts to utilize new materials are in the hands of promoters rather than under the guidance of established operators. The procedure referred to for use on wheat straw, which uses a countercurrent two-stage cook with the rod mill as a continuous digester for the first stage, has been found to be particularly applicable to bagasse and cornstalks.[7] The nonfibrous cellulose material produced is used as a stiffening agent in paperboard manufacture, and bleached cellulose fiber is used for light-weight and high-grade papers for numerous uses. Four tons of cornstalks or bagasse have been found to yield one ton of high-grade bleached cellulose fiber and one ton of the nonfibrous material mentioned above.[8]

4. Value of Annual Plants

In the manufacture of viscose rayon and staple fiber, purified straw pulp has found use in Germany in recent years. For cellulose esters, such as the nitrate and acetate, and cellulose ethers, such as the methyl and ethyl ethers, cotton linters and purified wood cellulose low in pentosan content are preferred. The pulps obtained from annual plants, especially cereal straws,[9, 10] which comprise the largest source of cellulose material collected

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[6] W. Raitt, *The Digestion of Grasses and Bamboo for Papermaking.* Crosby, Lockwood & Son, London, 1931.

[7] S. D. Wells and J. E. Atchison, *Paper Trade J.*, **112**, 34 (Mar. 27, 1941).

[8] S. D. Wells, U. S. Patent 2,181,556 (Nov. 28, 1939).

[9] S. D. Wells, *Ind. Eng. Chem.*, **21**, 275 (1929).

[10] E. Sutermeister, *The Chemistry of Pulp and Papermaking.* 3rd ed., John Wiley, New York, 1941.

as a step for the harvesting of a more valuable product, have a high pentosan content; where this constituent is unobjectionable, an enormous source of material is available.

The degree to which annual plant fibers can be used in paper manufacture depends upon the dimensions of the fibers, the proportion of fibrous to nonfibrous cells, and the physical properties of the fiber, rather than upon the chemical properties of the pulp. With the exception of the bast fibers of flax, hemp, ramie, etc., the pulps from annual plants are high in pentosans and hemicelluloses. The fibers hydrate on mechanical treatment more easily than wood pulps or rag fibers and, in general, these properties limit their use to papers in which the amount of mechanical treatment given to the pulps is comparatively mild. The retardation of free drainage on mechanical treatment (in some instances even pumping) interferes with the subsequent bleaching and washing operations, and with the formation and drainage of the sheet on the fourdrinier wire or cylinder mold, and with the removal of the water from the sheet on the presses. Consequently, weak brittle paper often results, or the rate of production of the paper machines may be retarded. With due consideration of these properties, however, annual plant fibers may contribute to the quality of the product or reduce cost of fabrication. They are not suitable, however, as general purpose pulps and should be used only in papers where they contribute definitely desired characteristics.

Cereal straws have been used as a source of cellulose fiber for paper and other products throughout the Christian era. The feasibility of their use depends entirely upon economic factors. Recent improvements in pulp purification will probably extend the use of straw, particularly for paper products to which its fiber will impart inherent desirable properties. The same may be said of grasses such as bamboo, bagasse, and cornstalks, the first of which is now the basis of a large industry in Burma. Utilization of the nonfibrous cells as a stiffening agent in ordinary paperboard further contributes to the feasibility of the use of annual plants as a source of cellulose fiber.

5. Fibrovascular Elements

Many fibers used in commerce and industry consist of filaments of indefinite length rather than individual fibers. These filaments are obtained by separating the fibrovascular elements of stems and leaves from the parenchyma tissue by means of scraping, beating, scutching, and combing, usually by hand. The product is valued principally for its strength, resistance to moisture, and its ability to be spun or twisted into cords or

coarse threads which can be used for rope, cordage, or twine and in coarse textiles, such as burlap, bagging, netting, matting, and hammocks. The filaments have essentially the same chemical composition as the original plant, and the presence of noncellulosic matter is not important insofar as it does not affect the durability, strength, or other physical properties of the product made therefrom. Their value for cordage is usually so much more than the prevailing price of paper stock that they are usually not considered as sources of cellulose.

Among the fibers in this class may be mentioned the following: abaca or Manila hemp and banana; sisal, henequin, and pita; New Zealand flax; caroa and pineapple; cabuja, Mauritius hemp, and fique; and palm leaves.

When these materials are subjected to the usual alkaline cooking treatments, the individual, ultimate fibers are liberated and the noncellulosic constituents are dissolved. The lengths of the ultimate fibers bear no relation to the lengths of the filaments from which they were derived. Sisal, for instance, yields a fiber not much longer than short-fibered hardwoods, such as poplar, beech, birch, or maple. Manila hemp and caroa, on the other hand, yield a very long and uniform fiber, capable of use in the manufacture of high-priced papers suitable for special uses such as tags, sandpaper, flour sacks, electric insulation, tea bags, stencils for mimeographing, and lens paper. These fibers do not fibrillate or hydrate on beating to the same extent that bast fibers, wood pulp, or rag fibers do, and papers made therefrom are characterized by an unusual combination of porosity, strength, resistance to wear, and wet strength.

Chapter VII

BLEACHING AND PURIFICATION OF CELLULOSE

BLEACHING AND PURIFICATION OF CELLULOSE

R. S. Hatch

The bleaching and purification of cellulosic materials, as at present practiced, are based on a historical development rather than on the application of a complete theory at any one time. In order to show the foundations of the present processes, it has been necessary, therefore, to give a survey of the stages of the development and the reasons for the changes introduced. Theory has been introduced wherever possible in order to justify these changes.

The bleaching process has as its objectives the removal of certain non-cellulosic compounds associated with cellulose in its natural state and the destruction of colored compounds which impart to the cellulose a distinct color.

A. BLEACHING OF CELLULOSE TEXTILES AND RAGS

1. Early History

Historically, the bleaching of linen textiles is probably as old as the art of weaving. In the process of washing unbleached linen, the ancients discovered that the action of sunlight gradually bleached the goods they were attempting to clean. This observation led to a definite bleaching art in which the goods were first washed with alkali obtained from the leaching of wood ashes and then spread on the grass and exposed to sunlight. This process was repeated many times until the goods had been bleached to a satisfactory white.

It is interesting to note that the bleaching of linen by the process just described, with some modifications, was the only known method of bleaching cellulose textiles for well over two thousand years. During the 18th century, the art of grass bleaching of textiles became almost a monopoly in Holland. Cloth woven in England, Ireland, Scotland, and Germany was shipped to Holland to be bleached. It was customary to ship the unbleached goods to Holland in the early spring to take advantage of the long

hours of summer sunlight. At best, the bleaching by sunlight was a slow and laborious process requiring seven to eight months of intermittent washing and exposure to the sun to produce a satisfactory product.

The discovery of chlorine by Scheele in 1774 marked an abrupt and rapid change in bleaching technology. It was Scheele who first noted the powerful bleaching action of chlorine on plant material. Scheele's experiments were extended and elaborated upon by Berthollet who discovered that chlorine gas, when absorbed in a solution of caustic potash, produced a liquor having powerful bleaching action. The commercial production of a potassium hypochlorite solution was first undertaken at Javelle in France, and the solution was known as eau de Javelle. A few years later, Labarraque replaced caustic potash solutions with caustic soda as the absorbing agent, and the solution he prepared was known as eau de Labarraque. In 1798, Charles Tennant of Glasgow obtained a British patent[1] for the production of a bleaching solution by absorbing chlorine in a suspension of lime in water. This patent was later successfully contested by several investigators, and Tennant lost his monopoly. However, in 1799, Tennant obtained a second British patent[2] which covered the preparation of a solid bleaching powder by subjecting calcium oxide to the action of chlorine gas.

The successful production of a solid, reasonably stable bleaching agent from chlorine and lime was the foundation of the great bleaching industry which was rapidly to follow.

2. Comparison of Different Celluloses

Cotton fiber, as it occurs in nature, is a relatively pure cellulose with which are associated only small percentages of fats, waxes, and coloring matter. On the other hand, cellulose which is obtained from wood and from many annual plants has associated with it relatively large amounts of both noncellulosic compounds and coloring matter, the removal of which greatly complicates the bleaching process.

When cellulose is isolated from wood by either an acid or an alkaline cooking process, an equilibrium is reached beyond which the more complete removal of the noncellulosic constituents results in a partial destruction and degradation of the cellulose. It is, therefore, customary to carry the cooking process only to a point where the optimum yield of an impure cellulose, suited to a particular purpose, is obtained, and then to rely on the bleaching process and on subsequent purification methods to produce a

[1] C. Tennant, Brit. Patent 2209 (1798).
[2] C. Tennant, Brit. Patent 2312 (1799).

finished cellulose of the desired color and quality. The same conditions prevail, to a somewhat lesser degree, in the isolation of cellulose from various annual plants which are used as a source of commercial cellulose.

This brief introduction to the consideration of the bleaching process brings out the significant difference between the bleaching of cotton fiber and the bleaching of cellulose obtained from lignified tissues.

3. Process and Agents

Cotton textiles are customarily produced from the raw cotton fiber. In the process of forming the cotton thread, or yarn, and in the subsequent textile operations, certain chemical compounds such as oils, or lubricants, are used as aids in the mechanical process. Also, a certain amount of soil and dirt is picked up in the mechanical processing of the fiber.

The finished unbleached cotton textile is delivered to the bleachery where the bleaching, dyeing, printing, or mercerizing operations are carried out. The first operation is known as "boiling out," and in modern bleacheries it is carried out in a pressure vessel known as a kier. The kier is a suitable closed vessel, capable of withstanding a moderate internal pressure, in which the unbleached cotton textile is packed and subjected to treatment, under pressure and at elevated temperature, with a caustic soda solution of sufficient strength to dissolve out the natural fats and waxes which are associated with the raw cotton fiber, together with chemical compounds which may have been added as aids to the spinning or weaving process. Upon completion of the boiling-out operation, the textile is thoroughly washed to remove the alkali and the dissolved impurities, and the washed goods are then subjected to the bleaching operation. This is commonly done in specially designed equipment with solutions of calcium hypochlorite or sodium hypochlorite. After the bleaching action, which is carried out with an alkaline bleach solution, has proceeded to the desired degree, the material is "soured," or rendered acid. The souring operation removes any inorganic compounds which may have been deposited on the fiber. Following this step, the goods may be treated with an antichlor to remove the last traces of chlorine, after which they are thoroughly washed. The bleached product is then ready for subsequent operations such as dyeing, printing, etc.

The hypochlorites of the alkaline earth or the alkali metals are still the most widely used bleaching agents for textiles. Their use has the greatest background of experience, and they are the lowest in cost. During the past decade, however, the use of hydrogen peroxide in alkaline solution has

found increasing favor. Marked advances in the successful production of high-strength hydrogen peroxide solutions of lower relative cost, as well as a more intimate knowledge of the dangers to be avoided in the use of this bleaching agent, have contributed to its increased use. One of the chief advantages of the use of hydrogen peroxide is that it leaves no chemical residues to be removed. Recently, the du Pont Company[3] has brought out a continuous process in which the goods pass continuously through an alkaline boil, a washing operation, a hydrogen peroxide bleach, and a final wash. It is claimed that this process greatly reduces time and uncertainty in the bleaching operation and produces a finished product of superior quality.[4]

4. Rag Half Stuff for Papermaking

Before the discovery of the sulfite process for the manufacture of chemical wood pulp in 1865, substantially all paper was made from cotton or linen rags or from straw and certain species of the grasses. Before the discovery of chlorine, the best papers were produced from sun-bleached cotton or linen rags. The discovery of the bleaching action of hypochlorites, however, opened up to the papermaker a vast new field of raw material in both new and old rags, whether unbleached, or bleached, and dyed. In the bleaching of rags, the papermaker followed the general practices established by the textile manufacturers. The rags, when received at the paper mill, were first sorted to remove foreign material such as wool, silk, buttons, etc. They were then cut into pieces of suitable size, packed in a cylindrical steel boiler, and usually a mixture of lime and soda ash was added. The boiler was then steamed while slowly rotating for a period of ten, twelve, or more hours under a pressure of ten to twenty pounds. At the end of the cooking period, the liquor was drained off and the boiler emptied. The cooked rags were then washed and partially defibered in a hollander washer. When the washing and defibering was completed, sufficient calcium hypochlorite solution was added and the bleaching was carried on for a period of one to three hours. After this, alum solution was added to render the contents of the hollander slightly acid. The partially bleached contents of the hollander were emptied into a "drainer," which was a rectangular enclosure usually built of brick and provided with a draining floor of perfo-

[3] T. W. Stephenson and D. J. Campbell, *The du Pont Mag.*, **35**, 6 (Oct., 1941).

[4] The reader who wishes a more detailed description of the apparatus and methods used in the bleaching of textiles is referred to J. Merritt Matthews, *Bleaching and Related Processes as Applied to Textile Fibers and Other Materials*. Chemical Catalog, New York, 1921.

rated brick, or tile, which allowed the excess weak bleaching solution to pass to the sewer. Drainers were usually built of sufficient size to hold the contents of several hollanders which were emptied in succession into the drainer until it was completely filled. After a draining period which varied greatly in different mills, but was usually at least a week, bulkhead doors on the drainer front were removed and the bleached half stuff was ready for subsequent papermaking operations. The "draining" period was a very essential part of the bleaching process, since the bleaching in the hollander was carried out at relatively low temperatures and low consistence. Sufficient excess bleach solution remained with the half stuff in the drainer to complete the bleaching action at very low chlorine concentration and with minimum damage to the cellulose.

The preparation of bleached rag half stuff just described has been the accepted method of bleaching rags for papermaking since the adoption of hypochlorites as bleaching agents. From time to time, rag merchants have attempted to produce bleached dry half stuff, but usually the process was speeded up and the bleached dry half stuff was usually much inferior to that produced by the paper mill.

5. Straws and Grasses

Straw and esparto fiber are cooked and bleached by a very similar procedure. The raw fiber is dusted and cut to a suitable length. It is then cooked with caustic soda, lime, or a mixture of lime and soda ash, after which the washing and bleaching duplicates the bleaching of rag half stuff. The cooking of cereal straws and of grasses removes most of the silica compounds and the cementing material to the degree where relatively small amounts of hypochlorite are required for satisfactory bleaching, although considerably more hypochlorite is required than is found necessary in the bleaching of rags.

B. BLEACHING OF ACID-COOKED WOOD PULP

The bleaching of chemical wood pulp presents a more difficult problem than the bleaching of rags or of cereal straws and grasses. The true resistant cellulose content of wood represents approximately 45 to 55% of the dry weight of the wood. The balance consists of water-extractive material, pentosans, hexosans, hemicelluloses, resins, fats and waxes, and lignin. As has been stated before, the cooking process removes a large part of these noncellulosic materials, but eventually an equilibrium is reached beyond which the more complete removal of these noncellulosic materials

results in decreased yield and lowered quality of the isolated cellulose. Therefore, any bleaching and purification process for chemical wood pulp must be considered from two points of attack: (1) the completion of the cooking process, which involves further removal of appreciable amounts of nonceliulosic material, and (2) the destruction of the coloring matter retained by the fiber.

This essential difference between chemical wood pulp and cotton cellulose was not fully appreciated by the papermakers who first attempted to bleach wood pulp. They naturally attempted to follow the general practice which had been used in the bleaching of rags; the only difference was that the alkali cooking step, as practiced with rags, was not used.

1. Early Methods

The procedure first practiced was to break up and defiber the unbleached wood pulp in a hollander washer, add bleach liquor, and, after a suitable time interval, empty into a drainer. The bleached pulp so produced was at first of poor color and quality. The percentage of hypochlorite required was many times that required for rags, and the bleaching time at the low temperatures and consistences normally used for rags had to be greatly extended with resulting lowered production. The next development was to increase the consistence in the hollander washer and materially to increase the temperature of the reaction by adding live steam to the contents of the hollander. This greatly speeded up the bleaching action. On account of the large amount of material rendered soluble by the bleaching action, it was found advisable to wash thoroughly the bleached pulp in the hollander and to arrest the bleaching action before emptying into the drainer. In this manner, a fairly satisfactory bleached pulp which met the requirements of the times was produced. Production was, however, limited because of the relatively small capacity of the hollander and limited capacity of drainers.

As a result of the production difficulties mentioned, the pulp mills themselves turned to the bleaching of their product. Instead of using hollanders and drainers, they first used large tanks equipped with agitators in which pulp was bleached at about 3% consistence and at elevated temperatures. At this low consistence, the time required for satisfactory bleaching was so long that for batch operation excessive tank capacity was required. The next logical step was the attempt to bleach continuously at system rate of production. Numerous ingenious methods of continuous bleaching were developed, but the inherent difficulties of control where bleachability

and consistence varied over a wide range prevented the general adoption of continuous low-consistence bleaching.

Since in bleaching at low consistence an exceptionally long time is required for the reaction to be completed at normal temperatures, and since the amount of steam required to heat a pulp suspension of low consistence to a temperature sufficiently high to speed up the reaction increases greatly the cost of bleaching, various adaptations of the hollander design, so constructed as to operate at considerably higher consistence, were devised. Of these many designs, the one which was most universally accepted both in the

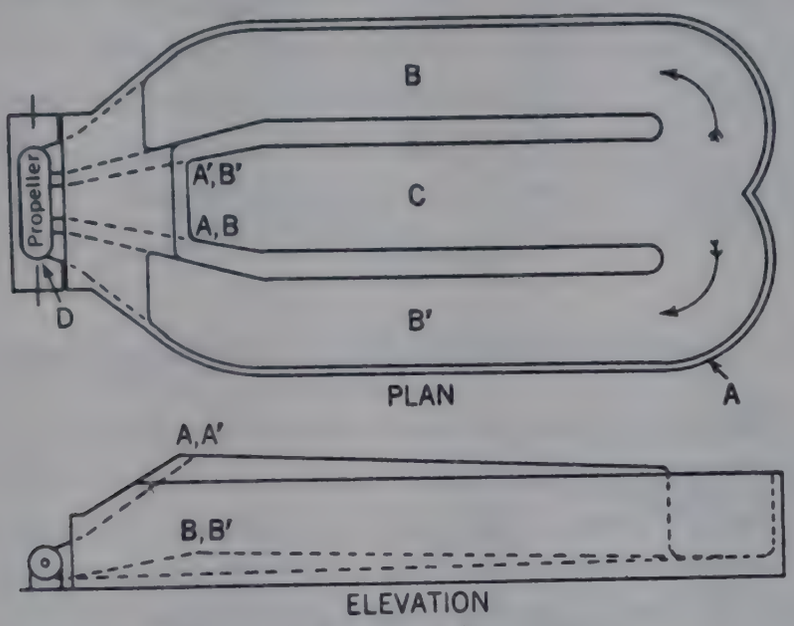


FIG. 1.—BELLMER BLEACHER.

A. Rectangular tile-lined concrete tub.
AB; A′B′. Tile-covered mid-feathers which divide tub A into three channels.
B, B′, C. Channels.
D. Mechanically driven propeller.

United States and abroad was first brought out by the Bellmer Brothers in Germany in 1896. There have been many minor changes in the design of the Bellmer bleacher, but the general principles of construction have remained the same. Figure 1 shows in plan and elevation the design of the Bellmer bleacher which has been in general use in the United States for many years. In Figure 1, A represents a rectangular stream-lined concrete tub equipped with a tile lining. AB and $A'B'$ are tile-covered mid-feathers which divide the tub A into three channels. At the end of tub A, located at D, is a suitable enclosed, mechanically driven propeller, the purpose of which is to circulate the pulp in tub A. In Figure 1, the circulation is shown by the arrows passing from the propeller to channel C and returning to the propeller through channels B and B'.

The pulp, water, and bleach liquor, in proper quantities to give the desired consistence, are fed into this apparatus until it is substantially full and the contents are circulated until bleaching is complete, after which the bleached pulp is washed out through suitable discharge valves and is pumped to suitable washing equipment.

With this bleacher, it is possible to operate at consistences as high as 7%. Under these conditions, the bleaching time is greatly decreased and very marked savings in steam result because of the higher consistence. Furthermore, there results a considerable saving in power required for circulation per ton of pulp bleached. Because of the much less space required for a given tonnage, the building cost is materially reduced.

Other advantages of the higher consistence were improved color, cleanliness, and quality of the finished pulp, as well as some saving in chlorine because lower temperatures resulted in less conversion of hypochlorites to chlorates.

2. Continuous Single-Stage Bleaching System

The many advantages observed as a result of increasing consistence stimulated investigation of methods for bleaching at still higher consistence and at lower temperatures. The first installation to operate successfully at 12% consistence was made, in 1912, at the Burgess Sulphite Mill of the Brown Company at Berlin, N. H., then under the management of Robert B. Wolf. Figure 2 is a schematic drawing of this equipment which was a continuous single-stage bleaching system operating at mill production rate. Cylindrical tanks were used in this bleaching system, three of which, *A*, *B*, and *C* are shown in Figure 2. In each tank was a heavy central shaft *E* to which was attached a series of arms *D* arranged to mix thoroughly the thick pulp. The first two tanks were connected at their bottoms by a closed pipe equipped with a screw conveyor to aid in the movement of the thick pulp from one tank to the other. Between tanks *B* and *C* was a similar pipe with screw conveyor to convey the pulp from the top of tank *B* into the top of tank *C*. These conveying devices alternated between the bottoms and tops of the tanks all the way through the series as shown. In operation, pulp thickened to the desired consistence, together with the bleach liquor, entered through a screw conveyor at point *F*. When tank *A* was full, the screw conveyor *G* was started, and feeding continued until tank *B* was filled. From tank *B*, the pulp discharged into tank *C* through conveyor *H;* when *C* was filled, the conveyor at *I* was started and the next succeeding tank was filled. At the high consistences

which were used in this bleaching operation, it was necessary to employ screw conveyors to carry the pulp from each tank to the next. The agitators in each tank served to effect a thorough and uniform mixing of the pulp under treatment in the particular tank. The size and number of these tanks were so chosen that at the consistence, time, temperature, and the

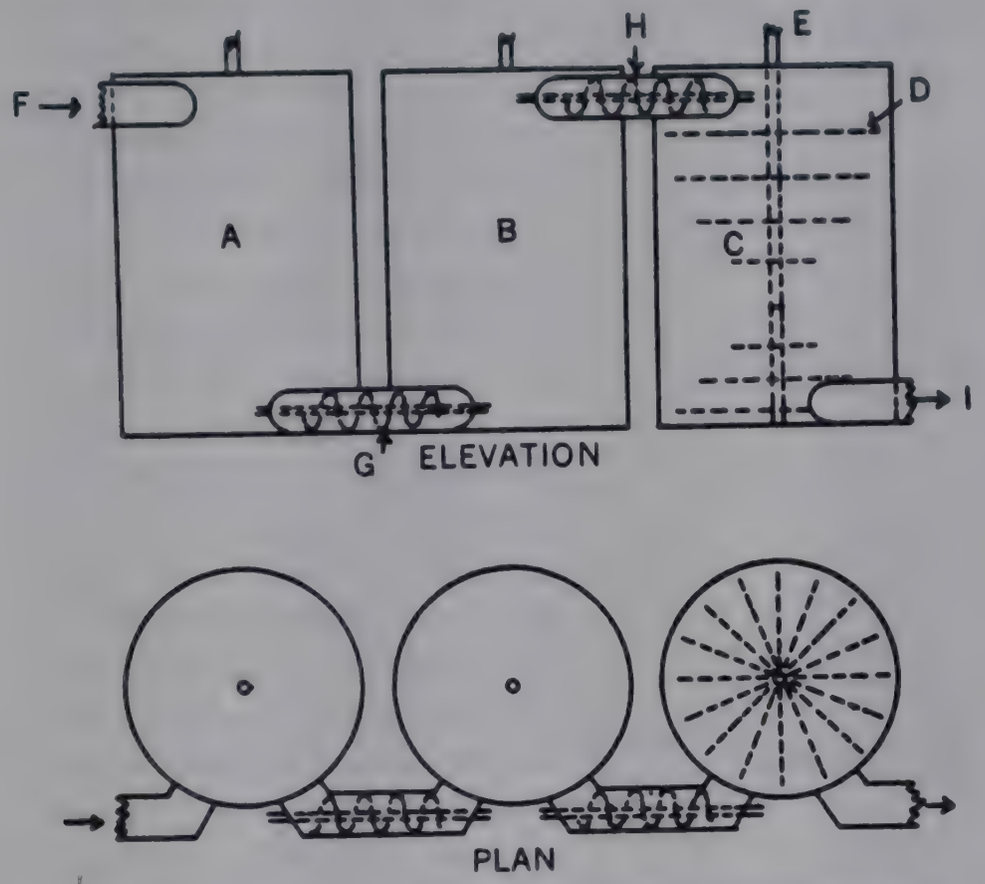


FIG. 2.—CONTINUOUS SINGLE-STAGE BLEACHING SYSTEM.

A, B, C. Bleaching tanks.
D. Shaft arms for mixing pulp.
E. Central shaft.
F. Screw conveyor for introduction of bleach liquor.
G, H, I. Screw conveyors for discharging pulp into succeeding tank.

system rate of flow, the pulp leaving the final tank was fully bleached and ready for the washing operation.

A very marked improvement in the cleanliness, color, and quality of the finished pulp, as well as further economies in steam, power, and space required, resulted from the introduction of this bleaching process.

3. Wolf Horizontal Bleacher

As a result of his experience with bleaching at higher consistence, Wolf set out to design a bleacher which would operate at still higher consistence.

The first bleacher of this type[5] was installed at the pulp mill of the Newton Falls Paper Company, at Newton Falls, N. Y., in 1921. The design of this bleacher is shown in Figure 3. It consisted of a rectangular concrete tank *A* provided with a partition *B*, which divided the tank into two equal rectangular channels *C* and *D*. In the bottom of each channel, twin screw conveyors, driven through a series of gears outside the tank, were arranged. The twin screw conveyors in each channel were designed to move the mass of high-consistence pulp in one direction in one channel and in the opposite direction in the other channel. At each end of the main structure and passing through a suitable opening in the partition *B*, was a smaller single screw conveyor *E* or *E'*; the speeds were so arranged that pulp would be transferred from channel *C* to channel *D* at the same rate at which it was driven lengthwise through either channel *C* or channel *D*. Thus, by adjusting the speeds of the various conveying screws, the thick mass of pulp was caused to circulate continuously in a rectangular path through channels *C* and *D* and the partition *B* while, at the same time, a complete turnover was being effected as a result of the difference in size and speeds of the screw conveyor systems.

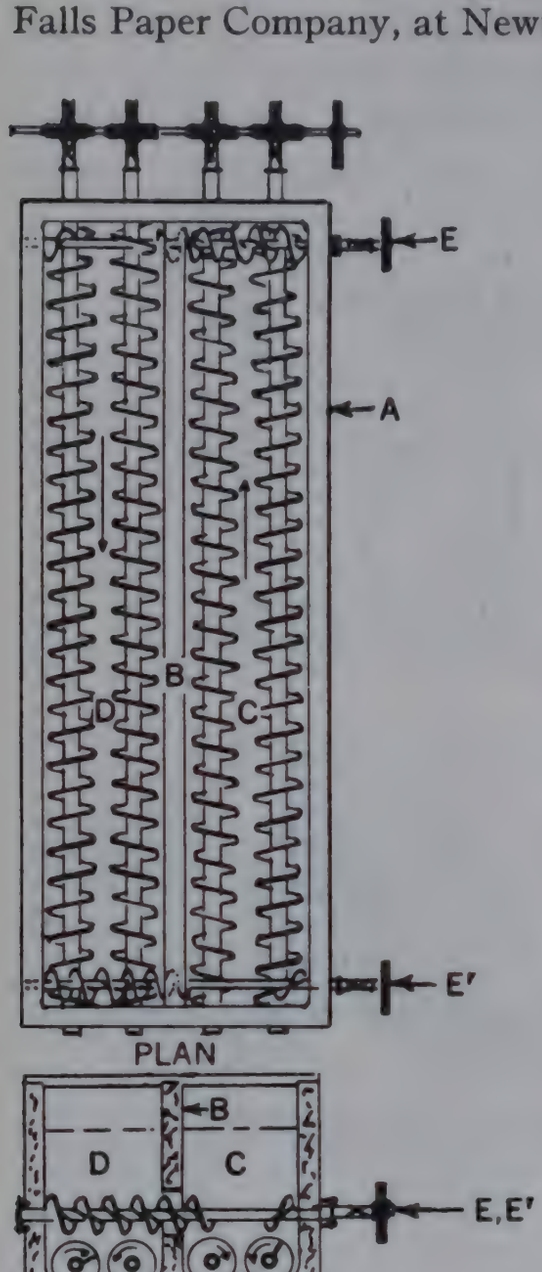


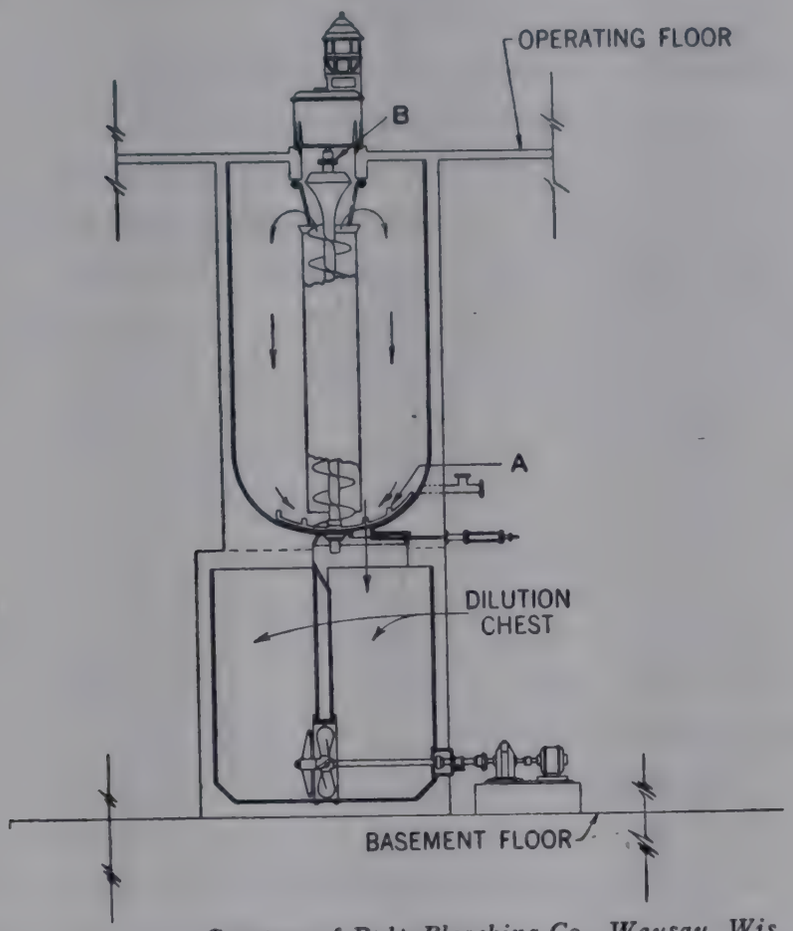
FIG. 3.—WOLF HORIZONTAL BLEACHER.

A. Concrete bleaching tank.
B. Partition.
C, D. Rectangular channels of equal volume.
E, E'. Screw conveyors.

It was possible, in this apparatus, to bleach at consistences from 15 to 25%. At these consistences, pulp takes the form of a wet mass of crumbs and no longer possesses the property of a fluid. Since the fibers are no longer free to move in a fluid medium, it is essential that the bleach liquor be very uniformly distributed and the reacting mixture frequently and thoroughly agitated to

[5] R. B. Wolf, U. S. Patent 1,433,865 (Mar. 13, 1922).

prevent nonuniform action of the bleach liquor on the fiber. This is accomplished in the Wolf horizontal bleacher by the combination of longitudinal and cross screws operating at different speeds, which effects a thorough turnover of the mass at each cycle in the circulation.



Courtesy of Pulp Bleaching Co., Wausau, Wis.

FIG. 4.—TYPE V W BLEACHER WITH DILUTION CHEST.

A. Plow designed to sweep close to bottom of tank.
B. Screw conveyor.

4. Type V W Bleacher

Shortly after the installation of the Wolf horizontal bleacher, a patent was granted to P. K. Fletcher[6] for a cylindrical vertical bleacher designed to operate at consistences of 16 to 20%. The manufacturing rights for this bleacher were acquired by Wolf and associates, and there followed a series of design modifications resulting in the modern Type V W bleacher (vertical Wolf bleacher) shown in Figure 4.

This bleacher consists of a tile-lined concrete tank with hemispherical

[6] P. K. Fletcher, U. S. Patent 1,466,499 (Aug. 28, 1923).

bottom in which is mounted a vertical shaft carrying a screw conveyor system *B* and a plow *A* designed to sweep close to the bottom of the vessel. A suitable drive mechanism is mounted on top of the bleacher and connected to the screw conveyor mechanism *B*. Openings are provided for the admission of pulp and the discharge of the finished bleached pulp to a suitable dilution chest beneath the bleacher.

It has been stated that pulp of 15% consistence no longer has the properties of a fluid. If pulp suspensions up to consistences approaching 4% are observed, it will be noted that the fibers move freely in the liquid when subjected to mechanical agitation. As consistence is increased, however, there is an increasing tendency for fluid to separate from the fiber at the point where mechanical force is being applied. For example, if a rod is passed through a 6% suspension of pulp, the pulp ahead of the moving rod dewaters and becomes of higher consistence, while the pulp behind the rod takes up the water liberated and becomes of lower consistence. The phenomenon just described is very marked at consistences varying from 10 to 20%. Beyond this higher consistence, it becomes less marked until a point is reached where extremely high pressures are required to force liquid from the fiber mass. Because the Type V W bleacher shown in Figure 4 operates best at 16 to 18% consistence, full advantage is taken of the tendency of pulp at that consistence to lose fluid upon application of mechanical force. The plough shown at *A* in Figure 4 is designed to overfeed the vertical screw conveyor *B*. Because of this design, fluid is forced out and the pulp passing up through the vertical screw conveyor is of higher consistence than the pulp in the main body of the bleacher. As the pulp is discharged from the top of the conveyor *B*, it mingles with pulp of lower consistence and absorbs sufficient liquid to come to moisture equilibrium. It will thus be seen that there is a constant turnover or exchange of liquid in the pulp mass. Furthermore, the sweeping plough at the bottom of the bleacher takes off a cross section of the descending mass of pulp with each revolution and, consequently, effects a constant turnover or mixing of the pulp. In this type of bleacher, therefore, conditions are favorable to constant and complete intermixing of both pulp and liquid, which makes for maximum uniformity of the bleaching action.

At the high consistence maintained in this bleacher, there is enough internal friction and squeezing action to break up fiber bundles and organic dirt particles, allowing the bleach solution to react more completely and thus produce a distinctly cleaner pulp. For single-stage bleaching, a bleacher of the size shown in Figure 4 has a capacity of about five tons. Under these conditions, the bleacher is first filled to about 80% of its cubic

capacity. During the bleaching cycle, the mass swells sufficiently to fill the bleacher to capacity. This swelling is due to the liberation of gas, principally CO_2, as the bleaching proceeds. The normal bleaching cycle for single-stage operation is four to six hours. The temperature rise due to internal friction is about 1°C. per hour, to which must be added the temperature rise due to chemical action. This will depend on the bleachability of the original pulp, but usually will amount to from 4 to 8°C.

When operating at these high consistences, it is not desirable to add steam if sufficient capacity has been installed. If the addition of steam is avoided, a pulp of improved physical and chemical qualities results. In order to keep temperatures as low as possible, a large number of Type V W bleacher installations were equipped with air ducts and blowers. These ducts discharged air over the surface of the pulp as it was discharging from the top of the vertical conveyor and served to keep temperatures down, especially during summer when mill water was at higher temperature.

5. Thorne Bleacher

About two years after the installation of the first Wolf horizontal high-density bleacher at Newton Falls, C. B. Thorne[7] of Canadian International Paper Company designed and put into operation a somewhat different type of high-density bleacher. Figure 5 shows the construction of this equipment.

It consists of a concrete tile-lined tower *A* near the bottom of which is located a suitably driven agitator *C* which aids in removing the bleached pulp through the discharge opening in the bottom of the tower. To secure even mixing of pulp, water, and bleaching liquor, a so-called "opener" *B* is provided. This opener has two shafts equipped with pins so arranged that the thickened pulp is torn apart and mixed with the bleach liquor and any necessary dilution water before the pulp is discharged into the tower *A*. The size of the tower *A* is so chosen that sufficient time is allowed for the bleaching cycle to take place before the pulp is discharged through the bottom opening to a suitable dilution tank.

In the Thorne bleacher, a continuous high-density operation takes place in which no agitation occurs except during the addition of the bleach liquor in the mechanical opener and during the brief period of discharge from the bottom of the tower. Many of the Thorne bleaching towers have been installed abroad, and on this continent several installations have been made in Canada and in the United States.

[7] C. B. Thorne, U. S. Patent 1,656,765 (Jan. 17, 1928).

It is recognized that, at consistences of 16 to 18%, too much agitation of the mass during the action of the bleach is to be avoided because of the damage which may occur to the fiber. Thorne sought to avoid mechanical action entirely during the bleaching, depending exclusively on thorough and rapid mechanical mixing of bleach liquor and pulp in the opener ahead of the tower. He also sought to cut down investment in batch equipment by using a continuous system.

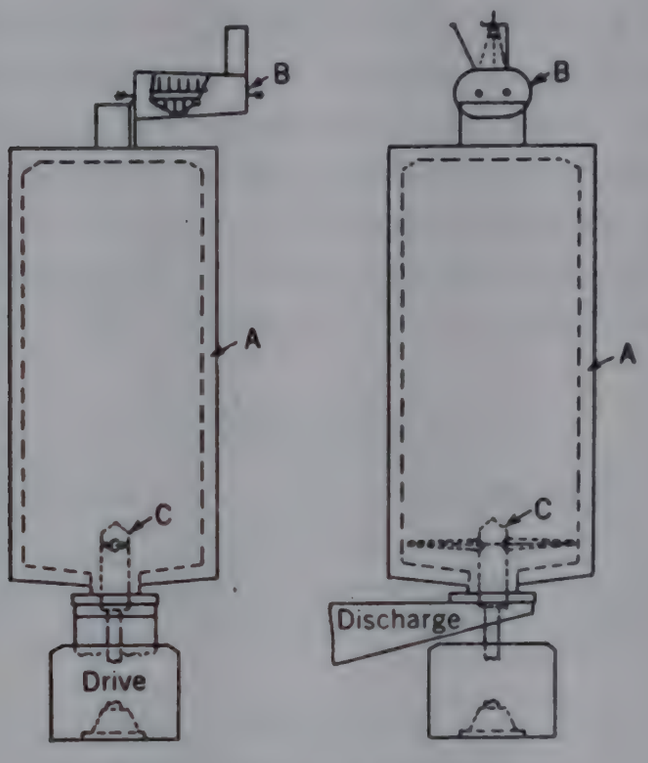


FIG. 5.—THORNE BLEACHER.

A. Concrete tile-lined tower.

B. "Opener" for uniform mixing of pulp, water, and bleaching liquor.

C. Agitator for discharging bleached pulp.

Since there is no mixing during the bleaching cycle and since sulfite pulp is never perfectly uniform in bleachability, it is not possible to secure, in a single-stage operation, as uniformly bleached a product as may be obtained where some agitation occurs during the bleaching cycle. If, however, the Thorne high-density continuous tower is followed by a second bleaching stage at lower consistence where there is adequate agitation, any lack of uniformity may be rectified in the second stage.

Many different types of high-consistence bleaching equipment have been designed and put into operation since the pioneering of Wolf in this field, but most of these have long since been abandoned. The two types of high-

consistence bleachers that have been generally and most universally accepted are the Type V W bleacher shown in Figure 4 and the Thorne bleacher shown in Figure 5.

C. MULTI-STAGE BLEACHING

Before the equipment used and the results obtained in multi-stage bleaching are discussed, it is advisable to consider the action of bleach liquor on chemical pulp. If, to a suspension of unbleached sulfite in water, sufficient hypochlorite for complete bleaching is added, the pulp first turns a dark red and then rapidly passes through a series of color changes. The dark red first observed changes to a lighter red and then through an orange to yellow, after which the change proceeds at a slower rate from yellow to white. If, at the stage when the pulp assumes an orange color, some of the liquor is squeezed out, it has a distinct brown color which gradually disappears as the pulp changes to a yellow color.

This peculiar behavior of pulp in the presence of bleach liquor led to the development of multi-stage bleaching, for it was assumed that, if the colored liquor resulting from the partial bleaching of the pulp to an orange color could be separated, there would result a saving in chlorine because chlorine would not be consumed in destroying the soluble color produced in the early stages of the bleaching action.

A study of the rate of chlorine consumption during the bleaching process shows that the reaction rate is very rapid at the start and then slows down to a marked degree. Figure 6 shows the chlorine consumption of a typical sulfite pulp, at four different consistences, plotted against time. These curves show that, even at low consistence, a large part of the hypochlorite is consumed in the first hour. The proponents of multi-stage bleaching assumed that, if just sufficient hypochlorite could be added to render the greater portion of the incrustants soluble without destroying the soluble colored compounds formed, a substantial over-all saving in hypochlorite would be accomplished without too great an investment in equipment, since the time required for this part of the reaction is relatively brief.

Much has been written by various investigators [8, 9, 10] concerning the savings in chlorine, yield, and physical and chemical qualities of pulp produced

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[8] E. Opfermann, *Wochbl. Papierfabr.*, **52**, 1643 (1921).

[9] B. Johnson and A. Parsons, *Pulp Paper Mag. Can.*, **26**, 671 (1926).

[10] G. P. Genberg and E. O. Houghton, *Paper Trade J.*, **88**, 71 (Apr. 25, 1929); 53 (May 2, 1929).

by multi-stage hypochlorite bleaching. Numerous installations were made, and considerable controversy arose as to the most desirable consistences at which to operate each stage as well as the correct percentages of total chlorine to be used in each stage. Chlorine savings, over single-stage operation, reported by different authors[11, 12, 13] ran all the way from 10 to 30%. The average savings, however, were close to 25%.

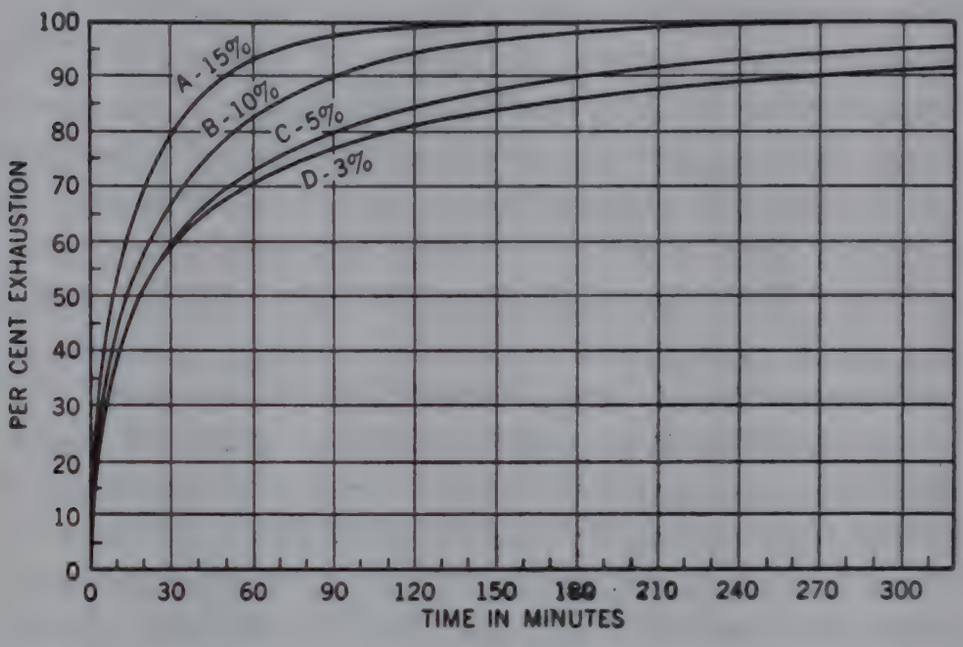

FIG. 6.—CONSUMPTION OF CHLORINE AS HYPOCHLORITE BY TYPICAL SULFITE PULP.

Curves are shown for four different consistences (3%, 5%, 10%, and 15%) over varying periods of time.

The change to multi-stage bleaching brought about a rather profound change in bleach plant design which greatly increased the capital cost of this phase of pulp manufacture. More bleaching units, more washing units, and usually a greater water consumption were required, and a slightly lowered yield of bleached pulp resulted, but the savings in chlorine and the improved physical and chemical qualities of the product fully justified the increased investment.

Multi-stage hypochlorite bleaching was destined, however, to be of rather short duration, for the ground was being prepared for a distinctly different approach to the bleaching problem. This new approach was based on the action of elemental chlorine on the noncellulosic residues re-

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[11] E. Heuser, *Paper Trade J.*, **91**, 55 (Aug. 14, 1930).

[12] R. S. Hatch, *Paper Trade J.*, **89**, 135 (Oct. 31, 1929).

[13] E. Hochberger, *Papier-Fabr.*, **26**, Fest- u. Auslands-Heft, 66 (1928).

maining in chemical pulps and leads to a consideration of the accepted modern methods of wood pulp bleaching.

D. CHLORINATION FOLLOWED BY HYPOCHLORITE BLEACHING

1. Chlorine Action on Noncellulosic Portion of Wood

For many years prior to the serious consideration of the use of elemental chlorine as a part of the bleaching process, the action of elemental chlorine on the noncellulosic portion of wood was well known. Cross and Bevan[14] in 1889 brought out their well-known analytical method of determining the percentage of cellulose in lignified tissues by alternate treatments with moist chlorine and sodium sulfite. It was well established that the lignin and certain other constituents of lignified tissues would readily combine with elemental chlorine to form chlorinated products which were soluble in sodium sulfite or in alkali. With sulfite pulp, there is a somewhat different reaction. As was mentioned early in this chapter, the cooking process, which renders lignin soluble, finally reaches an equilibrium beyond which attempts to remove more lignin are accompanied by degradation of the cellulose and a marked decrease in yield. However, the lignin which remains associated with the liberated cellulose no longer reacts with chlorine in the same manner as the native lignin of the wood. It is undoubtedly sulfonated for, upon chlorination, it is readily soluble in the acid chlorinating solution.

At this point, the statement just made should be somewhat modified by pointing out that the lignin residues present in the tracheid fibers of the wood substance are rendered soluble in acid solution by chlorination. This does not seem to be true for the residues present in the medullary ray fiber. It is well known that medullary ray fiber contains, beside lignin residues, a large percentage of resins, fats, and waxes. Analyses of isolated medullary ray fiber show an alcohol-ether soluble content which is about ten times that of the tracheid fiber. Whether the lignin also present is protected by these alcohol-ether soluble substances or is not sulfonated in the same manner as that present with the tracheid fibers is not definitely known, but it is known that the ligneous residues in the isolated medullary ray fiber do not, upon chlorination, become soluble to the same extent as similar residues in the tracheid fibers. Since, however, medullary ray fiber amounts to only 5 or 10% of the isolated wood cellulose, the insolubility of the chlorinated residues is of relatively little importance.

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[14] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **55**, 199 (1889).

2. Bleachability

In the following paragraphs, frequent reference will be made to "bleachability." For the purpose of this discussion, bleachability will be defined as the percentage of chlorine in the form of hypochlorite necessary, in a single-stage bleaching operation, to produce a pulp of a predetermined degree of brightness, as determined by any suitable reflecting spectrophotometer. The term bleachability is rather indefinite, since the amount of chlorine required to bleach to a given brightness will depend entirely on the type of pulp undergoing bleaching and the particular method of carrying out the bleaching process. The most universally adopted method of expressing bleachability in this country is the TAPPI Standard Method T 214 m-37. This method gives the chlorine equivalent of the amount of 0.03 *N* permanganate consumed in acid solution by one bone-dry gram of pulp in five minutes at 25°C. to which a correction factor is applied, depending upon the amount of permanganate consumed. The method is intended to give, approximately, the amount of chlorine in the form of hypochlorite necessary for the single-stage hypochlorite bleaching of the sample under consideration.

If unbleached sulfite pulp is suspended in water and chlorine gas is passed in or an aqueous solution of chlorine is added, the color of the reacting mixture first passes through the same range of color changes which is observed when a solution of hypochlorite is added to a suspension of unbleached pulp with this exception; when the pulp suspension reaches an orange color, the change in color from orange to yellow, in the case of chlorination, is a very slow reaction, while with hypochlorite the reaction is relatively rapid. Because of the great similarity in color reaction directly after the addition of either chlorine or of hypochlorite to an unbleached sulfite pulp suspension, and because of the further fact that both reagents form soluble colored compounds, it may be assumed that whether elemental chlorine or hypochlorite is used, the *first* reaction of either is one of chlorination. It is well known that, under certain conditions, hypochlorites act as chlorinating agents. The preparation of chloroform by the interaction of calcium hypochlorite and alcohol is an example of this. Another reaction is the formation of a monochloro derivative of hydroxybiphenyl according to the reaction[15]:

[15] E. F. Grether (to Dow Chemical Co.), U. S. Patent 1,832,484 (Nov. 17, 1931).

In Figure 7, is shown a typical curve in which the residual bleachability of a sulfite pulp is plotted against the percentage addition of the total chlorine required for single-stage bleaching. In developing this curve, elemental chlorine was bubbled into a pulp suspension at a fixed rate, and samples of the pulp, which was under constant and thorough agitation, were taken out at different points during the addition of the chlorine repre-

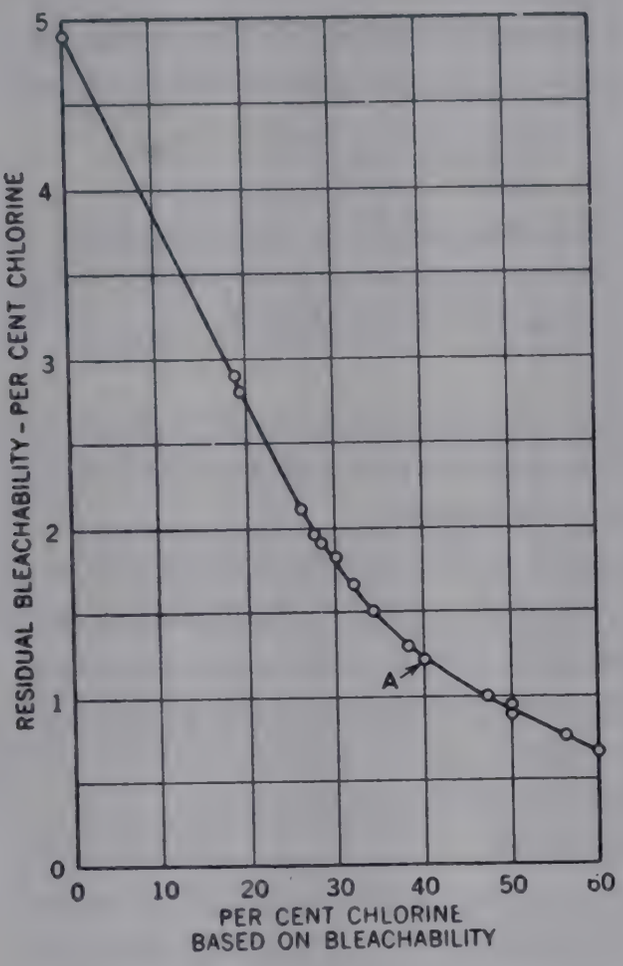

FIG. 7.—RESIDUAL BLEACHABILITY OF A SULFITE PULP VERSUS THE CHLORINE REQUIREMENTS FOR SINGLE-STAGE BLEACHING.

True chlorination reaction is approximately complete at point A. From this point on, oxidation begins to dominate.

sented by the abscissa in Figure 7. After thorough washing of the samples, the residual bleachability was determined and is represented by the ordinates in Figure 7. It will be noted that the slope of this curve begins to change sharply at a chlorine consumption representing approximately 40% of the original bleachability.

When chlorine is dissolved in water, the reaction which takes place is represented by the following equilibrium equation:

$$Cl_2 + H_2O \leftrightarrows HOCl + HCl \qquad (1)$$

In very dilute solutions of chlorine in water, the reaction goes decidedly to the right with the formation of hypochlorous and hydrochloric acids. If, however, there is organic material present which will readily combine, either by addition or by substitution, with chlorine, a chlorination reaction will dominate until chlorination begins to approach saturation thus:

$$RH + Cl_2 \rightarrow RCl + HCl \qquad (2)$$

The increasing concentration of HCl, resulting from the substitution reaction (2), will tend to drive reaction (1) to the left until substitution is complete. At this point the free hypochlorous acid in the solution may still act as an oxidizing agent.

Experience with the chlorination of sulfite pulp indicates that the true chlorination reaction is very rapid and that it reaches its completion approximately at point *A* in Figure 7. From this point on, the oxidation reaction begins to dominate. The foregoing analysis of the action of aqueous solutions of chlorine on sulfite pulp is intended to show the general directions of the reactions, and, while a sharp change occurs in the slope of the curve in Figure 7 at point *A*, representing about 40% of the chlorine requirement, both reactions do occur simultaneously, to some extent, though chlorination undoubtedly predominates up to point *A* and oxidation predominates beyond point *A*. A further consideration of the possible reactions which may occur when pulp is submitted to the action of elemental chlorine may be represented by the following equations:

$$RH + Cl_2 \rightarrow RCl + HCl \qquad (2)$$

$$>C{:}C< + Cl_2 \rightarrow >\underset{\displaystyle Cl}{\overset{\displaystyle |}{C}}-\underset{\displaystyle Cl}{\overset{\displaystyle |}{C}}< \qquad (3)$$

$$RH + Cl_2 + H_2O \rightarrow ROH + 2HCl \qquad (4)$$

$$R-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}H_3 + 3Cl_2 + 2H_2O \rightarrow RCOOH + 6HCl \qquad (5)$$

In Equation (2), which is straight substitution, half of the chlorine added will appear as HCl at the end of the reaction. In Equation (3), none of the chlorine will appear as HCl. In Equations (4) and (5), in which chlorine acts entirely as an oxidizing agent, *all* of the chlorine added appears at the end of the reaction as HCl. Many determinations of the amount of HCl

present at the end of the chlorination,[16, 17, 18, 19] related to the original chlorine added, have shown that between 50 and 60% of the chlorine originally added finally appears as HCl. The reactions given above, together with the sharp change in the slope of the reaction curve in Figure 7 at point *A*, seem to indicate that the first reaction is one of straight substitution which goes rapidly to saturation, at which point oxidation begins to take place more slowly.

Experiments have shown that if the pulp is chlorinated only to point *A*, the products of chlorination washed out, and the pulp subsequently, bleached with hypochlorite, the minimum amount of chlorine will be required to bleach to a predetermined white. While these experiments indicate that, under the conditions outlined, the minimum amount of chlorine is required for bleaching, this does not necessarily mean that chlorination should be carried only to point *A* from the viewpoint of practical operation and over-all economy.

In the discussion of single- and multi-stage bleaching, it was stated that with multi-stage hypochlorite bleaching it was possible to make savings in chlorine amounting to about 25% and to produce a pulp of better color and quality. It has also been stated that the first reaction of hypochlorites upon pulp during bleaching is probably one of chlorination. With hypochlorites, however, the chlorination reaction is relatively brief, and the chief reaction which predominates throughout is one of oxidation. Cross and Bevan showed that lignin could be removed from lignified tissues by chlorination followed by solution of the chlorinated lignin in hot sodium sulfite solution. Cellulose isolated by the Cross and Bevan method showed relatively little degradation as compared with that isolated by other methods. A comparison of the action of chlorine and of hypochlorite on sulfite pulp is shown in curves *A* and *B* of Figure 8. For the accumulation of the data which are graphically represented by these curves, a sample of pulp having a bleachability of 5.3% was taken. The total amount of chlorine used in each case was 3.45%, which represents 65% of the bleachability. This amount of chlorine was chosen because it is customary in batch chlorinating operations to chlorinate to 65% of the test bleachability.

Instead of bubbling gaseous chlorine into a suspension of the pulp in water, the necessary amount of chlorine, equivalent to 3.45% of the weight of the pulp, was first dissolved in water, and the pulp was added to this

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[16] E. Heuser and R. Sieber, *Z. angew. Chem.*, **26**, 801 (1913).
[17] P. Waentig, *Papier-Fabr.*, **25**, Tech.-wiss. Tl., 340 (1927).
[18] L. Rys, *Papier-Fabr.*, **26**, Tech.-wiss. Tl., 256 (1928).
[19] O. Kress and E. H. Voigtman, *Paper Trade J.*, **97**, 29 (Aug. 17, 1933).

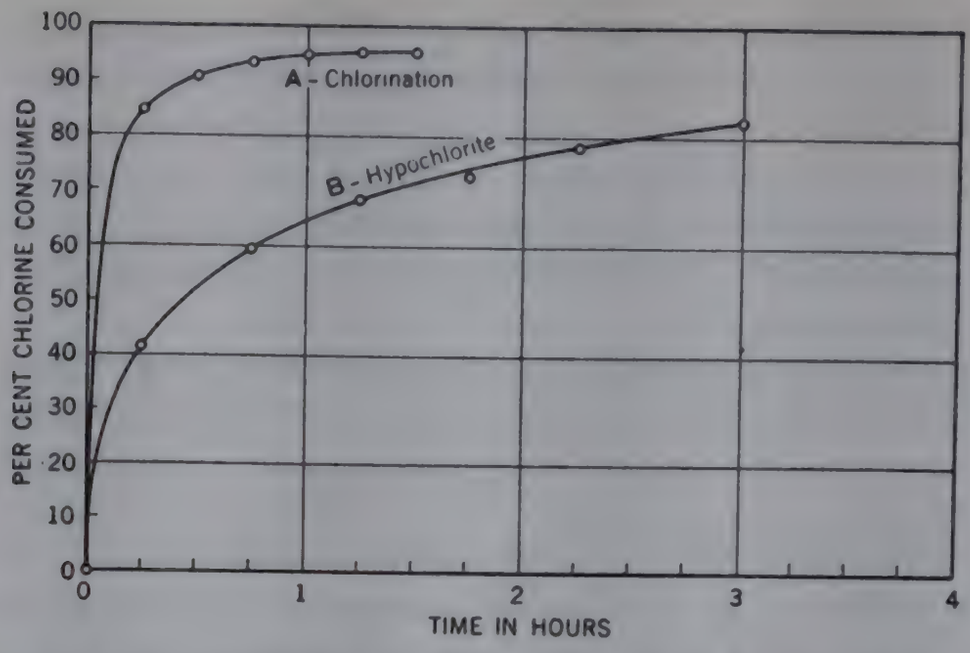

FIG. 8.—COMPARISON OF ACTION OF CHLORINE AND HYPOCHLORITE ON SULFITE PULP.

The bleachability of the pulp was 5.3%; the chlorine used was 3.45% in each case.

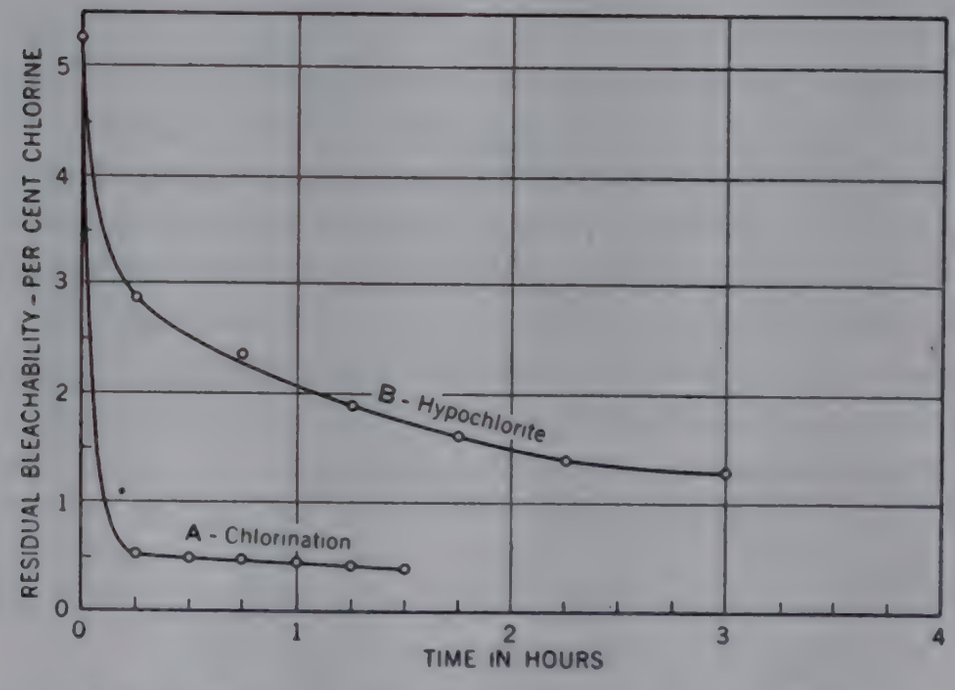

FIG. 9.—RESIDUAL BLEACHABILITY OF SULFITE PULP.

The points on these two curves are the same points indicated on the curves in Figure 8.

chlorine solution while agitating to obtain the best and most uniform distribution of pulp and chlorine water. These curves show the percentage of total chlorine consumed plotted against time. In the case of curve *A*, 91%

of the chlorine added is consumed in the first thirty minutes. At the end of one hour, the curve has flattened decidedly at 95% consumption, and further combination of chlorine with the pulp takes place very slowly. In curve *B*, only 52% of the total chlorine is consumed in the first half hour, and at the end of one hour the curve still has a reasonably sharp slope. A comparison of curve *B* with the exhaustion rate curve of pulp at 3% consistence in Figure 6 is interesting and shows plainly the effect of greater percentages of hypochlorite on the bleaching rate. Curves *A* and *B* of Figure 9 show the residual bleachability of the same sulfite pulp taken at the points indicated on the curves shown in Figure 8.

The four curves shown in Figures 8 and 9 indicate clearly the advantage of chlorination over hypochlorite in reducing the bleachability of a given pulp to a minimum in relatively short periods of time. It is obvious that pulp with such a low residual bleachability requires much less hypochlorite for final bleaching, and, consequently, much less degradation of the pulp may be expected in the final bleaching action because of the lower concentrations of hypochlorite necessary.

3. Quality of Bleached Cellulose

The quality of a bleached cellulose is determined to a large extent by the use requirements. For papermaking purposes, such physical properties as bursting strength, tensile strength, tearing resistance, and folding endurance are of the greatest importance to the paper manufacturer. For use in the manufacture of cellulose derivatives, the alpha-cellulose content,* copper number, 10% KOH solubility, and viscosity are more important considerations than the properties of value to the paper manufacturer.

There is, however, some relationship between viscosity and such properties as folding endurance, and it is customary for cellulose chemists to judge the amount of degradation which has occurred during the bleaching process by the reduction in viscosity which has taken place. Curves *A* and *B* of Figure 10 represent the viscosities in centipoises of a 1% solution of the sulfite pulps treated with chlorine and with hypochlorite, the viscosities having been determined on pulp samples taken at the points indicated on curves *A* and *B* of Figure 8. An examination of the two viscosity curves in Figure 10 indicates clearly the great advantage, as far as viscosity is concerned, in chlorination over hypochlorite oxidation as the first step in the bleaching process. Not only is a pulp of higher viscosity obtainable by this method, but also, in general, the physical characteristics of the pulp are

* Weyerhaeuser Timber Co. defines alpha-cellulose content as that portion of industrial cellulose pulp which is insoluble in 17.5% caustic at 20°C.

considerably improved by the chlorination-hypochlorite bleaching process over either single-stage or multi-stage hypochlorite bleaching. Furthermore, a considerable improvement in brightness is obtained for the same chlorine consumption when the former process is used.

Chlorination as a preliminary step has been shown to reduce pulp bleachability much more than does the action of hypochlorite. Furthermore, the physical and chemical properties of pulp which has been chlorinated as the first step are better than those of a pulp whose preliminary treatment has been with hypochlorite. For these reasons, there has been almost universal adoption of the method of bleaching pulps by first chlorinating under conditions which will give maximum exhaustion of the chlorine in a reasonably brief period, then thoroughly removing the soluble products of

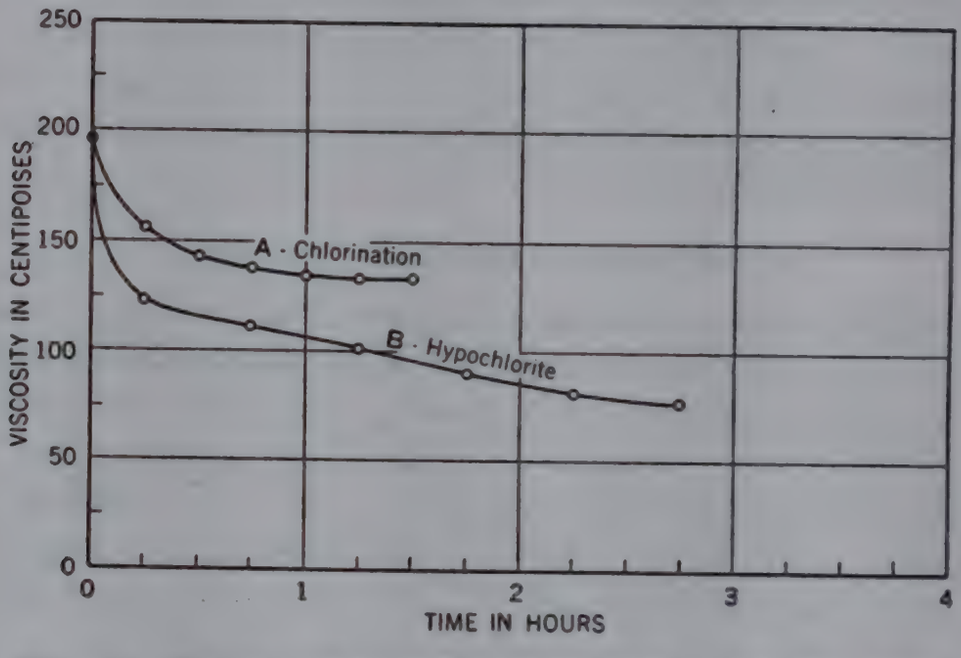

FIG. 10.—VISCOSITIES OF SULFITE PULPS TREATED WITH CHLORINE AND WITH HYPOCHLORITE.

The viscosities were determined on pulp samples taken at the same points indicated on the curves in Figure 8.

chlorination by washing, and finally bleaching the washed, chlorinated pulp. In this way, chemical pulp of the best physical and chemical quality is obtained with a minimum consumption of chlorine.

Referring again to chlorine consumption, it was pointed out, as a result of study of the curve shown in Figure 7, that the minimum chlorine consumption would be realized if the pulp were chlorinated to only 40% of the test bleachability instead of to 65%. However, if only 40% of the test bleachability is consumed in the chlorinating step, the residual bleachability of the pulp is somewhat higher than that obtained if the chlorination

is carried to 65% of the test bleachability. This requires a somewhat higher concentration of hypochlorite in the final bleaching stage, and more hypochlorite is required in this stage than is required when chlorinating to 65% of the test bleachability.

Since chlorine in the form of hypochlorite costs more than elemental chlorine, it has been found that the over-all cost of bleaching when chlorinating only to 40% of the test bleachability is greater than the over-all cost of bleaching when chlorinating to 65% of the test bleachability, even though less chlorine is used in the former case. Furthermore, the increased concentration of hypochlorite in the final bleaching stage which becomes necessary when chlorinating to only 40% of the test bleachability shows a distinct tendency to degrade the final bleached product more than is the case when the chlorination step is carried to 65% of the test bleachability.

4. Methods of Chlorination

The history of chlorination followed by hypochlorite bleaching reveals that the first attempts to follow this method were made by Watt and Burgess[20] working with a raw pulp made by the soda process. They demonstrated that a pulp of satisfactory quality could be produced in this manner, but the difficulties of generating and using chlorine at that time appear to have prevented the general adoption of the process, and no serious attempts were made to revive it until de Vains[21] proposed the process for bleaching sulfate pulp. About this time, the production and marketing of liquid chlorine on a large scale greatly stimulated interest in the use of elemental chlorine in the bleaching process. Drewsen[22] recommended its use for the production of pulps for nitration. Cataldi[23] brought out a process for the production of pulps from straw and grasses by a combination of chlorination, alkali extraction, and hypochlorite bleaching.

Two different methods of chlorination were recommended. One proposed to chlorinate the pulp at high consistence, that is at a consistence where all of the water present was absorbed by the fiber. At this consistence, the pulp, either in moist sheets or in crumbs, was subjected to the action of chlorine gas in closed chambers which were arranged for either intermittent batch operation or for continuous chlorination. The second method was to suspend the pulp in water at consistences varying from 2 to

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[20] C. Watt and H. Burgess, U. S. Patent 11,343 (July 18, 1854).

[21] A. R. de Vains and J. F. T. Peterson, German Patent 283,006 (Feb. 26, 1913); A. R. de Vains, U. S. Patent 1,106,994 (Aug. 11, 1914).

[22] V. Drewsen (to West Virginia Pulp & Paper Co.), U. S. Patent 1,283,113 (Oct. 29, 1918).

[23] B. Cataldi, Brit. Patent 101,475 (Sept. 11, 1916); French Patent 492,222 (1916).

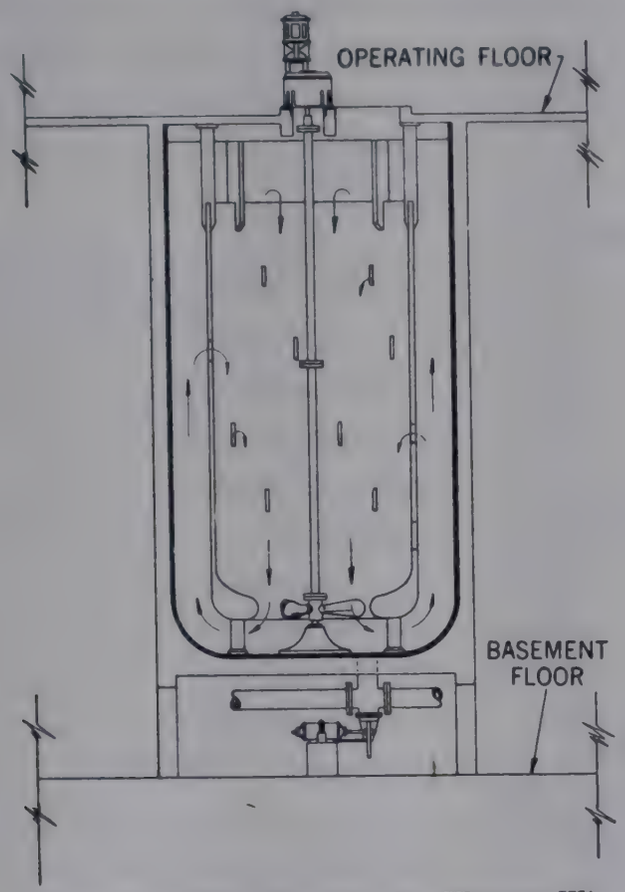
5% and to add either a solution of chlorine in water or bubble in chlorine gas through a suitable diffuser. The high-consistence method of chlorination now survives in the Cataldi-Pomilio[23] process for the production of cellulose from cereal straws, grasses, and some species of wood. The low-consistence process is used almost universally for the bleaching of pulp.

5. Low-Consistence Chlorination Process and Equipment

There are many modifications of the low-consistence process, some of which are batch chlorination and some continuous. Continuous chlorination is usually carried out in towers of sizes which are chosen to allow the required reaction time. In the continuous process, the chlorination usually is not carried as far as in the batch process because of the time required for complete exhaustion of the chlorine. It has been shown that about 40% of the total chlorine requirement of a pulp is exhausted very rapidly, after which the reaction slows down. In the continuous process, it is customary either (1) to add approximately 40% of the total chlorine requirement which is exhausted very rapidly and immediately wash the chlorinated product or (2) to add an excess of chlorine, allow it to react for five to thirty minutes, and then neutralize with lime or caustic soda, which converts the unreacted chlorine into hypochlorite, after which further time is allowed in a separate tank for the hypochlorite to be exhausted. The objection to the last-described modification is that the soluble colored products of chlorination are not removed prior to the addition of the alkali, and these colored products consume a considerable part of the hypochlorite which is formed when the excess chlorine is combined with alkali.

Figure 11 is the vertical elevation of a chlorinator which has been widely adopted in this country for the chlorination of both sulfite and sulfate pulp. The chlorinator illustrated has a capacity of approximately six tons of pulp at 3.5% consistence. It consists of a concrete tank lined with acid-proof tile. A draft tube, so chosen that the cross-sectional area is substantially one-half the cross-sectional area of the outside tank, is mounted within the outside tank and equipped with openings which allow a certain amount of cross circulation. A suitable propeller is mounted within the throat of the draft tube and arranged to circulate the pulp suspension downward through the draft tube and upward in the annular space between the wall of the draft tube and the wall of the outside tank. Gaseous chlorine is introduced through a suitable nozzle, or nozzles, located in the throat of the draft tube at a point where the velocity of the pulp suspension is highest. These chlorinators are arranged to circulate and turn over the entire contents of the chlorinator about once every two minutes. Under

these conditions, excellent dispersion of the chlorine in the pulp suspension is secured, and rapid and uniform chlorination of the contents is obtained. There are many other modifications of batch chlorinators, some of which have a design similar to that just described; others employ external pumps or other circulating means for the circulation of the pulp suspension and introduction of gaseous chlorine or chlorine dissolved in water. These modifications in design have no significant effect on the chlorination process as such and have been designed mainly to suit peculiar manufacturing conditions.



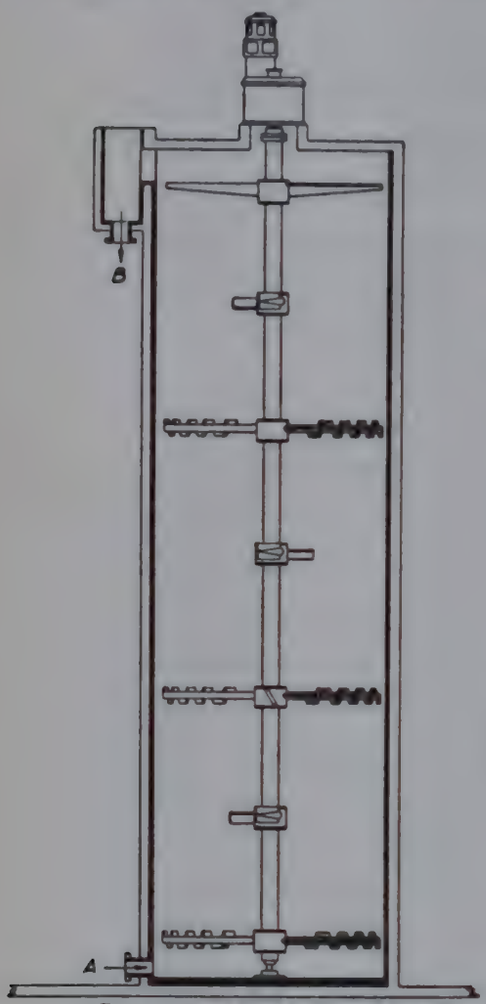
Courtesy of Pulp Bleaching Co., Wausau, Wis.

FIG. 11.—TYPE V L CHLORINATOR.

This chlorinator has been widely adopted in this country for the chlorination of both sulfite and sulfate pulps.

Continuous chlorination is usually carried out in towers to which the pulp suspension is metered, and to this metered pulp suspension is added either a metered flow of chlorine gas or chlorine water. These towers must be of a size sufficient to allow proper reaction time for whatever system rate of pulp flow exists. Pulp usually enters the bottom of the tower through a mixing device, fills the tower, and then overflows to the washing equipment. Such a tower is illustrated in Figure 12. The pulp suspension, mixed with the desired amount of chlorine, enters at *A*, and is periodically mixed by

the agitating arms which are equipped with blades so designed as to secure an intimate mixing of the pulp suspension as it rises through the tower. The chlorinated pulp suspension is discharged at point *B* and goes to the washing equipment. As was mentioned, there are other types of chlorinators which are designed for a much shorter exhaustion time, and the partially chlorinated pulp, containing more or less excess chlorine, is neutralized with lime or caustic as it leaves the tower, from which it goes to a chest or tank in which the hypochlorite, formed by combination between the added alkali and the unreacted chlorine, is allowed to react until it is exhausted.



Courtesy of Pulp Bleaching Co., Wausau, Wis.

FIG. 12.—CONTINUOUS CHLORINATOR.

A. Point at which the pulp suspension mixed with chlorine is introduced.

B. Point at which the chlorinated pulp suspension is discharged.

6. Value of Chlorination as Step in Bleaching Process

A consideration of the curves shown in Figures 8, 9, and 10 clearly indicates the value of chlorination as a step in the bleaching process. Chlorination proceeds rapidly to a maximum point, and any further reaction is extremely slow. At the point where maximum chlorine consumption is reached, a pulp of minumum residual bleachability is obtained. The curves under discussion were obtained with a pulp of 5.3% bleachability. Experience has shown that pulps with considerably higher bleachability or pulps with lower bleachability, when chlorinated to the optimum point, will all give chlorinated pulps with about the same residual bleachability. On the other hand, the action of hypochlorite, while at first very rapid, quickly slows down, and the residual bleachability is relatively high. As has been stated before, probably the first and very rapid part of the hypochlorite curve is one which is due in large measure to chlorination. The chlorination, however, persists for a relatively brief time, and then the reaction becomes mainly one of oxidation. A further important difference between the chlorination and hypochlorite reactions is the relatively small drop in viscosity of chlorinated pulp. This pulp shows

a nearly constant viscosity after the point of optimum chlorination has been reached, while the viscosity curve for pulp treated with hypochlorite not only shows a much greater drop in viscosity but also this drop continues to increase with time as the oxidation proceeds.

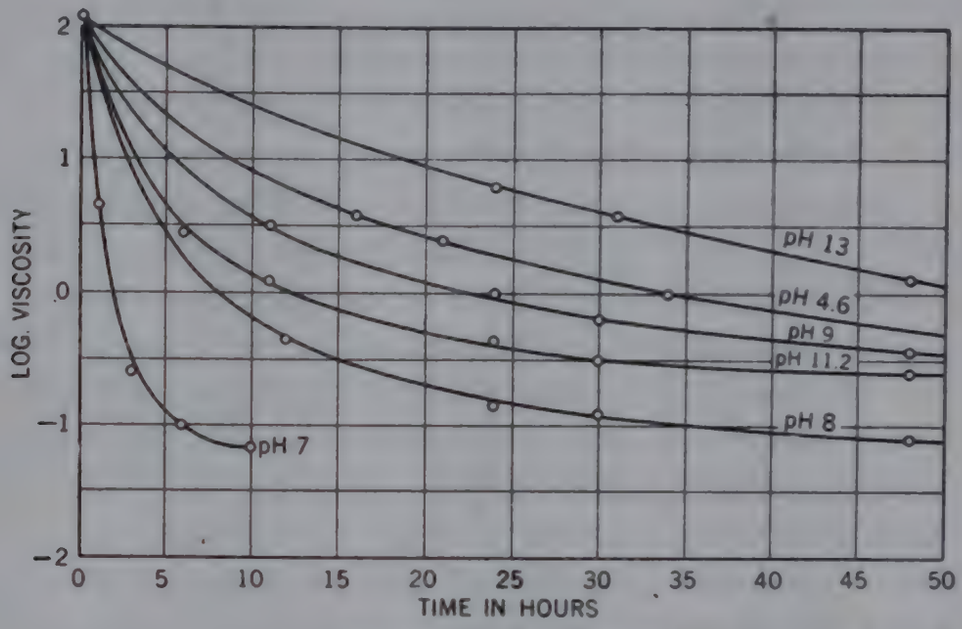
Before the introduction of chlorination as part of the bleaching process, there were many sulfite pulps on the market which were given the designation of "unbleachable." These pulps had a high bleachability, and attempts to bleach them with hypochlorite resulted in so much degradation that they were not considered suitable for the production of a bleached pulp. After the chlorinating step was introduced, however, it was found that these so-called unbleachable pulps could be readily bleached after chlorination to a satisfactory white without a serious loss in the physical and chemical properties. Many writers who have studied the action of chlorine on pulp have been accustomed to thinking of chlorine as an oxidizing agent, because of its strong oxidizing properties when existing in the form of hypochlorites, and have failed to consider the action of elemental chlorine as almost entirely a chlorinating rather than an oxidizing action. The behavior of elemental chlorine when brought into reaction with pulp is so sharply different from that of hypochlorites that the reactions which occur should in no sense be considered as bleaching reactions. It would be best to consider them as extensions of the cooking process in which the residual lignin is removed from the cellulose by virture of the formation of soluble chlorine compounds, especially in the case of sulfite pulp. Lignin analyses of thoroughly chlorinated sulfite pulps show only very small percentages of lignin left after chlorination. As stated earlier in this chapter, there is a sharp difference between the character of residual lignin left, after cooking, in the medullary ray fiber as compared with the tracheid fibers. Pulp from which all of the medullary ray fiber has been mechanically separated by fractionation shows substantially no lignin residues after thorough chlorination and washing. Such is not the case with pulp from which the lignin residues are removed by hypochlorite. The lignin is progressively attacked by the hypochlorite, but at no point in the hypochlorite reaction is there a sharp break in the lignin content of the pulp undergoing bleaching as occurs in the case of chlorination.

Thus it will be seen that if chlorination is carried to the optimum point, substantially all of the noncarbohydrate material, in the case of sulfite pulp, is removed in the subsequent washing of the chlorinated product. The only task left for a subsequent hypochlorite bleaching is the removal of coloring matter adsorbed by the cellulose fiber. This requires a relatively small amount of hypochlorite, and the bleaching problem begins to approach

that of cotton bleaching where, after the alkaline boiling out, adsorbed color is about the only material which requires oxidation for its destruction.

7. Effect of pH and Concentration

In any bleaching process where small amounts of colored residues are left associated with the cellulose, great care must be taken to carry out the bleaching process under conditions of concentration and *p*H which will have the least damaging effect on the final bleached product. The action



Courtesy of D. Van Nostrand Co., New York, N. Y.

FIG. 13.—RATE OF CHANGE IN VISCOSITY OF COTTON CELLULOSE PRODUCED BY HYPOCHLORITE SOLUTIONS OF VARYING *p*H (DORÉE[24]).

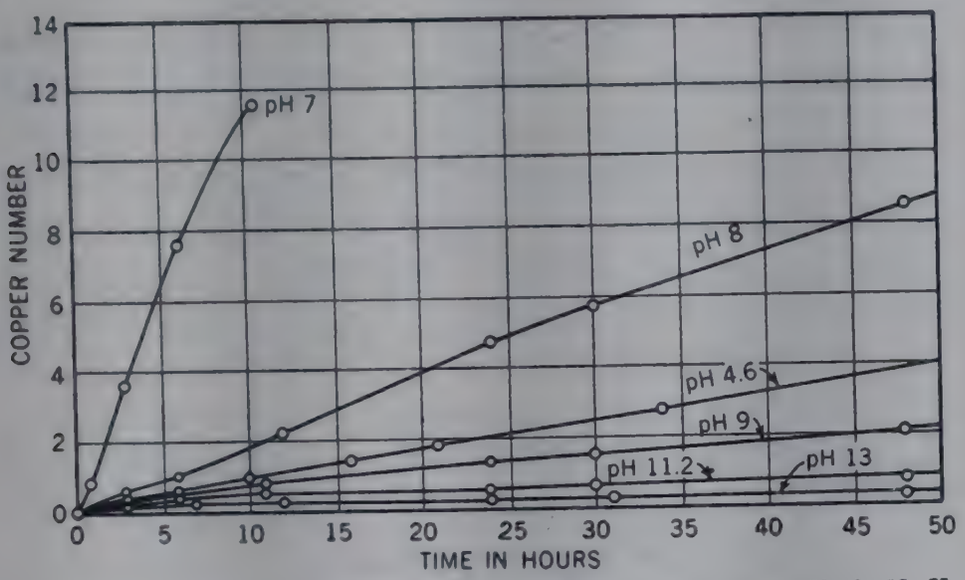
of hypochlorites on cellulose which has associated with it considerable amounts of noncarbohydrate material seems to be less drastic as long as there exists appreciable quantities of noncellulosic material which may be selectively oxidized. As this noncellulosic material disappears, an increasingly larger surface of pure cellulose is subjected to the action of the oxidizing agent, and the danger of degradation increases. It is necessary, therefore, in the bleaching of thoroughly chlorinated pulp to maintain the best possible conditions of temperature, concentration, and *p*H in order to secure a product having optimum physical and chemical properties.

In the bleaching of textiles, it has long been known that best results were obtained under either distinctly alkaline conditions, or under acid condi-

[24] C. Dorée, *The Methods of Cellulose Chemistry*. Van Nostrand, New York, 1933, p. 141.

tions within a certain narrow range and that the most damage and tendering of textile fibers occurred under conditions approaching neutrality. Dorée,[24] working with strongly buffered hypochlorite solutions ranging from a *p*H of 13 to a *p*H of 4.6, obtains some very interesting curves, two series of which are shown in Figures 13 and 14. These curves show that, from the point of view of increased copper number and decreasing viscosity, the action of hypochlorite at *p*H 7 is most drastic. In the *p*H range from 9 to 13 and at a *p*H of 4.6, the degradation is relatively small.

Until the introduction of the glass electrode as a means of measuring the *p*H of oxidizing and reducing solutions, exact control of the hypochlorite bleaching stage was difficult. Experience, however, had shown that if the



Courtesy of D. Van Nostrand Co., New York, N. Y.

FIG. 14.—RATE OF CHANGE IN COPPER NUMBER OF COTTON CELLULOSE PRODUCED BY HYPOCHLORITE SOLUTIONS OF VARYING *p*H (DORÉE[24]).

alkalinity of the pulp undergoing hypochlorite bleaching was kept high enough to give a momentary red color with phenolphthalein throughout the bleaching cycle, the quality of the resulting pulp would be considerably better than it would be if the alkalinity were allowed to go to a point where the addition of phenolphthalein to the bleaching mass would show no momentary red color. Without means of controlling the *p*H, however, bleaching time was very difficult to control because with increasing alkalinity the bleaching time was very materially increased and a great deal of uncertainty existed. With the introduction of the glass electrode, however, it was possible to make studies of the drop in *p*H during the bleaching action and to adjust the initial *p*H so that bleaching could be accomplished without drastic degradation of the pulp and within reasonable time limits.

A study of the reaction products resulting from the hypochlorite bleaching of wood pulp was made by Rashback and Yorston.[25] They measured the amount of CO_2 which was formed during experimental bleaching and also determined the approximate amount of organic acids produced. Their experiments showed that about 75% of the total reaction product was CO_2 and about 25% organic acids. Since the products of reaction of hypochlorites in the bleaching reaction tend to reduce the alkalinity during bleaching, it has been found necessary to add either sufficient excess alkali or a suitable buffer at the beginning of the bleaching process to prevent the *p*H, for any considerable time during the bleaching action, from approaching a value of 7 where the most destructive action on the cellulose occurs. Yorston[26] investigated the use of magnesium oxide as a buffer in bleaching, and his experiments indicated that better color and better physical and chemical properties could be obtained by bleaching under buffered conditions which maintained a *p*H in the vicinity of 10. Numerous other investigators have studied bleaching with buffers capable of maintaining other *p*H ranges, but the general custom in the commercial bleaching of wood pulps has been to use sufficient alkali in the form of either caustic soda or lime to keep the *p*H of the pulp during bleaching definitely above a *p*H of 7. It is well known that excess alkali sufficient to raise the *p*H to 11 or 12 greatly slows down the action of a hypochlorite. However, if enough excess alkali is not used, the *p*H will drop rapidly during the bleaching cycle due to the formation of CO_2 and organic acids. It is possible to maintain a *p*H range which will give satisfactory bleaching time and which, at the same time, will avoid a drop in *p*H toward the end of the bleach to a point where appreciable degradation occurs. It is possible to start with a relatively rapid action of hypochlorites in the earliest part of the bleaching cycle. During this part of the cycle, the greatest amounts of CO_2 and organic acids are produced with the result that the *p*H drops rapidly and the reaction speeds up accordingly. It is customary to regulate the alkali at the beginning of the final bleaching stage so that this part of the process will take place in from three to four hours at temperatures not exceeding 30°C.

8. Effect of Temperature and Consistence

If bleaching temperatures do not exceed 30°C., it is necessary to bleach at relatively high consistence in order to keep the time within reasonable

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[25] *Quart. Rev. Forest Products Laboratory of Canada*, No. 7, 12 (July–Sept., 1931).

[26] *Quart. Rev. Forest Products Laboratory of Canada*, No. 6, 80 (April–June, 1931).

imits. There has been a considerable difference of opinion among operators as to the ideal consistence at which to carry on the final bleaching action. Some favor a relatively low consistence with increased temperature and longer time, while others favor a high consistence at lower temperature and shorter time. With high consistence, where the pulp is no longer in a fluid condition, it is, of course, necessary to have thorough periodic mixing of the mass in order to secure uniform distribution of the bleaching agent. The internal friction which results from the periodic mixing of high-consistence masses of pulp definitely tends to break up chlorinated fiber bundles and expose them to the action of the hypochlorite. This assures a relatively cleaner product than may be obtained at low consistences where the pulp suspension acts as a fluid, and there is little mechanical action to aid in breaking up fiber bundles. At the higher consistence, the hypochlorite concentration is considerably higher, and, therefore, it is possible to bleach in a shorter time and at lower temperatures. For any given consistence, an increase in temperature greatly accelerates the bleaching action and at the same time accelerates the degrading action on the isolated cellulose. It is highly desirable, therefore, to choose a consistence and temperature at which, for a given alkalinity, the final bleaching process may be accomplished in a time which will be economically practicable, will secure a uniform bleaching action, and produce a pulp of optimum physical and chemical properties. It is obvious that with the variables of consistences, alkalinity, time, and temperature, all playing important roles in the bleaching cycle, it is possible to obtain satisfactory results for any given type of pulp over a reasonably wide range of conditions which may be met in any particular operation.

By choosing the proper *p*H range, consistence, temperature, and time of bleaching, it is possible, by suitable control of these variables, to produce finished products possessing quite a wide range of physical and chemical properties from the same raw material. The best bleaching method will be governed by the use requirements of the finished product and the equipment available for the bleaching process.

E. BLEACHING OF ALKALINE-COOKED PULPS

The alkaline process which is most universally used in this country today is the sulfate or kraft process. A certain amount of pulp is still being produced by the soda process, but the tonnage is relatively insignificant, and the conditions which must be met in the bleaching of sulfate pulps exist to a lesser degree in the bleaching of pulps cooked by the soda process. The

discussion of the bleaching of alkaline-cooked pulps will, therefore, be confined entirely to the problems arising in the bleaching of pulps produced by the sulfate process. It is to be understood that the same conditions will prevail to a lesser degree in the bleaching of pulps produced by the soda process.

The bleaching of pulps which have been cooked by alkaline processes follows, in general, the procedure which is used in the bleaching of pulp cooked by the sulfite process. The equipment and the various steps in the process are similar, but some of the reactions which occur differ quite sharply from those which occur in the bleaching of sulfite pulps.

It has been shown that, when sulfite pulp is chlorinated, the main portion of the chlorinated pulp is readily soluble in acid solution and that almost all of the lignin residues may be removed in soluble chlorinated form if the chlorination is carried sufficiently far.

When a suspension of sulfate pulp is chlorinated, the pulp passes through a series of color changes closely resembling those which take place during the chlorination of sulfite pulp. There is a marked difference, however, in the nature of the chlorinated compounds formed. The products of chlorination of sulfate pulp are much less soluble in acid solution than the corresponding products of sulfite pulp. Chlorination to saturation reduces the original test bleachability of the pulp, but this test bleachability is reduced by only about 60% as compared with 80 to 90% in chlorination of sulfite pulp. Reduction in the bleachability of sulfate pulp by chlorination is not so much due to the solubility of the chlorinated products in the acid solution as it is due to a change in the character of the lignin residues resulting from chlorination which requires less oxidation for destruction of the chlorinated product. Because these chlorinated residues do not readily go into solution in an acid medium, it has been found necessary to resort to alkaline extraction for their removal. Extraction with cold dilute alkali, while capable of removing a portion of the chlorinated product, has been found to be very inefficient. Treatment with dilute solutions of caustic at elevated temperature, however, renders these chlorinated compounds quite soluble. It seems possible that the chlorinated lignin residues in sulfate pulp are highly polymerized and that the treatment with hot alkali is necessary to break down these highly polymerized products to a point where they will go into solution.

The alkali metal salts of chlorinated lignin residues have a very high tinctorial power and are extremely dark in color. Although it is possible to remove the bulk of these alkali salts, after a hot alkaline extraction, by washing, sufficient colored, difficultly bleachable residues remain to give

the pulp a very dark color. Whatever the nature of these chlorinated residues may be, they appear to be very strongly adsorbed by the cellulose fiber, and their complete removal requires drastic bleaching action. This bleaching must be done very carefully, however, to prevent degradation of the cellulose during the process. It is usually carried out in several stages by alternate treatments with hypochlorite and alkali in order to obtain maximum brightness and desirable physical properties in the finished product.

There is a method by which these bleaching difficulties can be avoided, however. After a sulfate pulp has been chlorinated to the saturation point, it is possible, by mild and carefully controlled oxidation, to alter the structure of these chlorinated compounds so that subsequent treatment with hot alkali does not give the deeply colored alkali salts which are formed by treatment of the unoxidized chlorinated product with alkali. Provided the oxidation directly after chlorination is mild and carried out at sufficiently high pH, little damage is done to the cellulose, and the subsequent alkaline extraction and final bleaching of the pulp is rendered comparatively simple. Hypochlorite has been used for the required mild oxidation at high pH.

Early attempts to bleach sulfate pulp with hypochlorite alone gave very unsatisfactory results. It was found impossible to bleach sulfate pulp to a satisfactory white by hypochlorite alone, either in single- or multi-stage processes, without drastic degradation of the bleached product. It was not until de Vains[21] investigated a combination of chlorination followed by hypochlorite bleaching and demonstrated the possibility of producing a satisfactory quality of bleached sulfate pulp that any extensive bleaching of this type of pulp was undertaken. During the last twenty years considerable progress has been made in the production of fully bleached sulfate pulps of satisfactory physical and chemical qualities. There have been many modifications of the multi-stage bleaching process, and the technique of sulfate bleaching is still in a state of considerable flux.

Multiple chlorination has been advocated, but no particular advantages are gained by this modification. Since the products of chlorination are largely insoluble, multiple chlorination merely complicates the processes and usually requires more chlorine to accomplish the same result that may be obtained by a single chlorination to the point of saturation. The evidence further indicates that no improved physical or chemical properties are obtained by a multiple chlorination as compared with a single chlorination to saturation.

As is the case with the commercial bleaching of sulfite pulp, there exist many differences of opinion among operators as to the most desirable

methods of bleaching sulfate pulp to obtain a product of optimum physical and chemical properties. As an example, however, the following process may be cited as one which gives an excellent quality of finished pulp.

The pulp is first chlorinated with an amount of chlorine equivalent to 65 or 70% of the test bleachability. The chlorinated pulp is thoroughly washed to remove all of the acid formed and then subjected to a hypochlorite bleach at a *p*H of approximately 11. The amount of chlorine as hypochlorite is from 60 to 70% of the test bleachability of the chlorinated pulp. The pulp is then washed and given an alkaline extraction with caustic soda at a temperature of 60 to 70°C., the amount of caustic soda which is used ranging from 1 to 2% of the pulp undergoing extraction. This caustic extraction is preferably done at high consistence to avoid an excessive use of steam for heating. Agitation of the alkaline pulp at these elevated temperatures in the presence of air is to be avoided as much as possible, because of the degrading effect of atmospheric oxygen upon cellulose in a strongly alkaline medium. The hot caustic extraction usually requires about an hour, after which the pulp is washed and subjected to one or two hypochlorite bleaches at a *p*H between 8 and 9 and at temperatures not exceeding 33°C. if the bleaching is done at high consistence. After the final bleach, the pulp is usually suspended in water and acidified with SO_2, then it receives a final washing.

The Technical Association of the Pulp and Paper Industry has recently published a monograph entitled "Bleaching of Sulphate Pulp" by F. Loeschbrandt.[27] Loeschbrandt has made a very thorough study of the variables which affect the bleaching of sulfate pulps. This monograph follows the established practices of European sulfate mills and is recommended to those interested in this subject.

F. WASHING OF PULP

Both bleached sulfite and bleached sulfate pulps tend to show color recession over a period of time following the bleaching operation. The color recession of bleached sulfate pulp has, in the past, been much greater than bleached sulfite and has been one of the great difficulties which the bleached sulfate manufacturer has sought to overcome. Within a short period of time after manufacture, the color recession of both sulfate and sulfite pulps is most rapid. In the course of one or two months after manu-

[27] F. Loeschbrandt, *Bleaching of Sulphate Pulp.* Tech. Assoc. Pulp & Paper Ind., New York, 1941. This is a translation by E. Martin of an article published in *Kaymr Nachrichten*, No. 2–4, 1939.

facture, the rate of color recession becomes much slower, and after this period relatively little recession occurs.

The well-known complicated structure of wood fibers is probably responsible for the difficulty in washing out decomposition products resulting from the bleaching process. Not only must the decomposition products which exist on the surface of the fiber be thoroughly removed in the washing process, but also time must be allowed for the diffusion of these decomposition products out of the minute pores and canals existing as part of the fiber structure. More and more attention is being paid to so-called soaking periods in the bleaching process which allow time for this diffusion to take place. Probably one of the reasons why multi-stage bleaching operations of both sulfite and sulfate pulps yield finished products which show relatively little color recession is the repeated washings with large amounts of water, which give more opportunity for the decomposition products to diffuse into the washing medium.

The importance of water free from large amounts of heavy metals is beginning to be fully realized by pulp manufacturers. The strong tendency of cellulose to adsorb heavy metals from aqueous solutions makes it imperative to have sources of water relatively free from heavy metals if successful bleaching and washing are to be expected.

G. MISCELLANEOUS BLEACHING AGENTS AND PROCESSES

The large-scale development of the electrolytic process for the production of chlorine and caustic soda in this country has so reduced the price of chlorine that hypochlorite is probably now, and will continue to be, the cheapest oxidizing agent available. Also, elemental chlorine has given the industry in one substance an agent both for the extension and completion of the cooking process and for the subsequent oxidation which accomplishes the final bleaching. Therefore, it seems quite certain that chlorine will be the major bleaching agent employed by pulp manufacturers for some time to come.

1. Catalyzers for Hypochlorite

Many attempts have been made to use various catalyzers to speed up the action of hypochlorite in the bleaching process. The general experience has been that, while the addition of substances such as nickel salts, copper compounds, and others appears to increase the speed of the oxidizing action, they will at the same time have a destructive effect on the cellulose which is not apparent when hypochlorites are used alone. The presence

of copper salts seems to exert a specially degrading action when present during hypochlorite bleaching, and, because of the alkaline conditions under which hypochlorite bleaching is now generally carried out, these copper salts tend to become adsorbed by the cellulose fibers. If such bleached cellulose is to be used for subsequent manufacture of chemical derivatives, the presence of even minute amounts of copper will tend to act as a degrading agent in the future processing.

2. Hydrogen Peroxide

It was pointed out in the discussion of the bleaching of textiles that hydrogen peroxide is now being used to a considerable extent in the bleaching of cotton. Provided no metal catalyzers, such as iron or copper, are present, hydrogen peroxide may be used with considerable success and, since it leaves no heavy metal salts to be removed in the subsequent washing process, it has proved, for textiles, to be a very valuable bleaching agent. The cost of the active oxygen in hydrogen peroxide is, however, much higher than the cost of the equivalent amount of active oxygen in the form of hypochlorite. Since the bleaching of wood pulp requires relatively large amounts of oxygen as compared to textiles, the cost of hydrogen peroxide makes its general adoption in the bleaching of pulp almost prohibitive. The same is true for substantially all of the other well-known oxidizing agents. In general, the cost is higher and the results obtained are no better from the standpoint of color and quality than may be obtained by the use of hypochlorite under the proper control conditions.

3. Sodium Chlorite

An exception should be noted in the recently proposed use of sodium chlorite as a supplementary bleaching agent. White and Vincent[28] compare the bleaching action of sodium chlorite and hypochlorite and give data showing superior results which have been obtained in comparative bleaches with these two oxidizing agents. One interesting phenomenon in the use of chlorite is that, in many cases when chlorite is used as a final bleaching stage in a multi-stage operation, the viscosity is definitely increased while obtaining a higher brightness. This observation has been confirmed by a number of workers in the field and in this respect chlorite seems to be quite unique.

At the present time, the cost of sodium chlorite, based on its actual oxi-

[28] J. F. White and G. P. Vincent, *Tech. Assoc. Papers*, Ser. **24**, 571 (1941).

dizing power, is very much higher than that of chlorine in the form of hypochlorite. It is, therefore, out of the question to use chlorite as the principal oxidizing agent after chlorination, but it is possible, where certain special pulp characteristics are desired, to use it as a final step in a multi-stage bleaching operation.

H. BLEACHING AND PURIFICATION OF PULP FOR SPECIAL PURPOSES

During the last twenty years, there has been a steadily increasing demand for a highly purified alpha-cellulose made from wood pulp. This demand has been stimulated because of the greatly increased production of artificial filaments such as rayon, cellulose acetate, staple fiber, etc., all using cellulose as a raw material. In the viscose process for the manufacture of rayon, cellulose from wood pulp has been the chief raw material

1. Permanent Papers, Viscose, and Cellulose Derivatives

For the manufacture of permanent papers, the paper manufacturer relied for many years on new cotton rag cuttings or mixtures of cotton and linen cuttings, as well as upon old cotton rags. The introduction of many new types of synthetic fibers into the manufacture of textiles has made the problem of rag sorting and preparation increasingly difficult for the paper manufacturer because regenerated cellulose fibers, or cellulose derivatives, cannot be used successfully in papermaking. Furthermore, the paper manufacturer has become accustomed to the use of wood pulp as a major raw material. Because of the fact that wood pulp requires radically different processing methods than does rag fiber, the use of highly purified alpha-cellulose pulps from wood as a substitute for rag fibers in permanent papers has steadily increased.

In the viscose process, the first manufacturing step is the treatment of raw cellulose with mercerizing solutions of caustic soda, the excess of which is pressed out in the steeping tanks until the cellulose remaining has combined with it the necessary amount of caustic soda for subsequent processing. This steeping process, in a mercerizing solution of caustic soda, in itself acts as a purification process, and much of the alkali-soluble carbohydrate material is removed in solution in the steeping liquor. Up until about ten years ago, a wood pulp having an alpha-cellulose content of 86 to 87% successfully met the specifications of the viscose manufacturer. Since that time, however, specifications have required increased alpha-cellulose content for viscose manufacture until today most of the wood

pulp going into the manufacture of viscose has an alpha content well above 90%.

Up to the present time, it has been customary to produce cellulose esters and also generally the ethers from cotton cellulose made from purified cotton linters. The greatly increased production of cellulose derivatives, however, has caused increasing emphasis to be placed on the use of alpha-cellulose from wood pulp for the manufacture of these derivatives as well as for the manufacture of rayon and staple fiber by the viscose process.

2. Preparation of Highly Purified Alpha-Cellulose from Wood Pulp

As a result of the trends just mentioned, there has been great activity centered in the commercial production of highly purified alpha-cellulose from wood pulp. In discussing this subject, no attempt will be made to go into the detail of the many proposed processes which have appeared in recent years. The student of this subject is referred to an excellent review of the patent literature by Jayme.[29] An experimental study of the alkaline refining of wood pulp was made by Rys and Bonish[30] who have covered the recognized types of refining which will be discussed in the following paragraphs.

The substances which accompany alpha-cellulose in unbleached wood pulp may be divided into two classes: (1) the carbohydrates and (2) the noncarbohydrates. Of the carbohydrates, there are the pentosans, hexosans, hemicelluloses, uronic acids, oxycelluloses, and partly degraded cellulose which may possibly be included in the class of hemicelluloses. The noncarbohydrate portion is made up of lignin residues, fats and waxes, tannins, coloring matter, and inorganic ash.

The bleaching process, if carefully conducted, removes most of the noncarbohydrate material with the exception of the inorganic ash. Usually the inorganic constituents of pulp are made up of some silica, alkaline earth compounds, and residues of some of the heavy metals such as iron, manganese, and copper. Some of these metals are present as salts of inorganic acids, but in general the metal is bound to the cellulose, neutralizing carboxyl or sulfuric acid groups bound to the cellulose or an insoluble impurity therein. The heavy metals such as those just mentioned may exist in the original wood or may be introduced in the manufacturing process. While it is not possible to remove all the inorganic constituents of a bleached pulp by any commercially practicable process, it is possible to

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[29] G. Jayme, *Paper Trade J.*, 106, 37 (May 26, 1938).

[30] L. Rys and A. Bonish, *Paper Trade J.*, 108, 31 (May 11, 1939).

reduce greatly the inorganic ash content by a proper acid treatment during and after the final stage of bleaching. One of the advantages in the chlorination of pulp is that considerable amounts of hydrochloric acid are formed in the chlorinating process, and this acid dissolves the bulk of the inorganic material which subsequently may be washed out after chlorination. It is then only necessary to avoid the introduction of further amounts of inorganic material during the balance of the bleaching and purification process.

If the bleaching process is properly conducted, most of the lignin present in the unbleached pulp is removed or destroyed during bleaching. Some wood species, however, contain relatively high percentages of resins, fats, and waxes. Although these are partially removed in the bleaching process, it is necessary in the production of purified pulps for special purposes to effect a more complete removal of these compounds through special purification processes. The main problem, therefore, in the preparation of purified alpha-cellulose from wood pulp is, in addition to the purification which naturally occurs in the bleaching process, the removal of carbohydrate material other than alpha-cellulose and certain amounts of residual noncarbohydrate compounds not removed in the bleaching operation.

The generally accepted method of removal of these products which accompany alpha-cellulose in the original unbleached sulfite is some type of alkaline treatment either before, during, or after the bleaching process itself. Two general methods of alkaline treatment have been widely investigated and put into commercial practice. The one involves treatment of the pulp with relatively small amounts of alkali at elevated temperatures which range from 100 to 140°C. The other method involves treating the pulp cold or at moderately elevated temperatures with alkaline solutions of relatively high concentrations. For the latter method of treatment, the temperatures range from below normal room temperature to temperatures in the vicinity of 50 to 80°C., and the strengths of caustic soda, the alkali most commonly used, will range from a concentration of 3 or 4% to a concentration of as high as 20%.

3. Hot Alkali Treatment of Pulp

Of the two processes just mentioned, the treatment of wood pulp with dilute solutions of alkali at elevated temperatures was the first to be put into commercial operation. This process was based on the treatment of the unbleached pulp, or pulp in a partially purified condition, at a consistence of 5 to 10% with solutions of 0.5 to 2% caustic soda content. In this process,

the temperatures employed ranged from 100°C. at atmospheric pressure to 125°C. at the corresponding elevated pressure. At first, unbleached pulp was given the hot dilute caustic treatment, after which it was washed and subsequently bleached. It was discovered, however, that frequently treatment with alkali at these elevated temperatures, while raising the alpha content of the treated pulp, made it more difficult to bleach. For this reason, more recent practice has been either to chlorinate or partially to bleach the pulp before subjecting it to the hot alkali treatment.

The treatment of pulp by the hot dilute alkali process yields an alpha-cellulose specially suited for the manufacture of permanent-type papers where the alpha-cellulose is used as a substitute for rag pulp. The chief reason for this is that, with the concentration of alkali used and at the elevated temperatures, scarcely any swelling or mercerization of the fiber takes place. Cellulose fiber which has been mercerized is no longer suited to the manufacture of paper because it reacts differently to the mechanical beating process than does the normal cellulose fiber.

The hot alkali extraction process will give a pulp having an alpha-cellulose content of 92 to 95%. The yield of finished alpha-cellulose is, however, considerably lower than would be expected when the alpha-cellulose content of the original pulp is considered. Starting with pulps having an alpha-cellulose content of 86 to 88% in the original unbleached state, the yields obtained by the hot dilute alkaline extraction will vary between 70 and 80% based on the original pulp. It is apparent that considerable degradation of the alpha-cellulose takes place in the extraction with hot dilute alkali, with a resulting decrease in the yield of finished alpha-cellulose. This low yield is compensated for, to some extent, by the fact that no attempt is made to recover the alkali which is used in treatment when employing the hot dilute alkaline extraction. On the other hand, when employing the so-called cold process, or mercerizing process, the high concentrations of caustic soda used make it essential to recover the alkali. This greatly complicates the purification process and adds considerably to the investment in the purification plant.

There are many variations of the hot dilute alkaline process of refining in which relatively small percentages of caustic are used and in which temperatures are not carried as high as those previously mentioned. These processes involve, generally, the preparation of pulp for special purposes in which no attempt has been made to reach maximum alpha content. For example, there are many such processes used in the preparation of pulp for the manufacture of viscose. Such pulp is usually cooked to a relatively low bleachability, and the refining takes place as an intermediate step in the

bleaching process where the chlorinated, or partially bleached, pulp is treated at temperatures between 50 and 100°C. with just sufficient alkali to raise the alpha content to a point required by the specification. After washing, the chlorinated alkali-treated pulp is then bleached with hypochlorite under carefully controlled alkaline conditions to produce a satisfactory color. In refining treatments of this character, the loss in yield is not as great as results from the treatment with somewhat more alkali at 100°C. or at elevated temperatures and pressures. The net yield from the wood, however, is usually relatively low because pulps cooked to the low bleachability necessary for this type of refining suffer a material loss in yield in the cooking process itself. The net result is that the final yield of finished refined pulp is very close to that which would be obtained if a pulp of higher bleachability and greater yield in the cooking process were refined at temperatures of 100°C. or higher, with a somewhat higher concentration of caustic soda.

4. Cold Alkali Treatment of Pulp

The so-called cold, or mercerizing, process depends on the use of relatively high concentrations of caustic soda solution. Caustic soda solutions of from 5 up to 18% concentration have a very marked swelling action on cellulose at normal temperatures. This swelling increases with caustic concentration up to approximately 18%, beyond which little more swelling takes place. Pulp which has been swollen by strong caustic solutions in the refining process is no longer suitable for the manufacture of paper. Consequently pulp which has been refined by strong alkaline treatment at lower temperatures is only suitable for the manufacture of cellulose derivatives, and in many cases is not suited for this latter purpose until it has been given further stabilizing treatments.

Refining with caustic solutions of higher concentrations results in an almost theoretical yield of alpha-cellulose from the unbleached cellulose used as a raw material. Relatively little degradation occurs in the treatment with strong alkali solutions provided the treatment is properly conducted. It is, of course, necessary to carry on the strong alkali refining of pulp as much as possible in the absence of atmospheric oxygen since cellulose in a highly swollen condition and in the presence of atmospheric oxygen is readily degraded. The best methods of treatment with strong alkali solutions involve the use of closed vessels. Before introducing the mixture of pulp and alkali, the air is completely displaced by steam, or an inert gas, to prevent the degrading action of atmospheric oxygen. Upon comple-

tion of the treatment, the alkali must be washed out with minimum exposure of the pulp to oxygen until the greater portion of the alkali has been removed.

In the discussion of the hot dilute alkaline extraction, it was stated that finished pulps with an alpha-cellulose content of from 92 to 95% could be produced by this process. The strong alkali treatment will yield pulps of higher alpha-cellulose content ranging from 94 to 98%. In a refining process of this type, in order to assure a finished product of high alpha-cellulose content, it is not possible to follow the alkali treatment immediately with wash water without some lowering of that content. Dilution of the strongly alkaline extraction liquor tends to precipitate the dissolved carbohydrates, and it has been found necessary to weaken the alkali progressively in order to obtain a finished product of maximum alpha-cellulose content. A process patented by Papeteries Navarre[31] endeavors to overcome this difficulty by a countercurrent extraction method in which the pulp undergoing purification is treated in a series of tanks with caustic solutions of progressively lower strength until all of the extracted carbohydrates and impurities have been removed. By operating on a countercurrent principle, the strong caustic solution becomes increasingly contaminated with extracted products on passing through successive batches of untreated pulp, until the concentration reaches a point where recovery is necessary. Likewise, the countercurrent principle of washing produces wash liquors of high concentration and relatively low organic content which are suitable for further extraction.

The addition of reducing agents to the strong caustic treating liquors has been recommended, and definite advantages appear to be obtained when these reducing agents are added. Among these reducing agents, sodium sulfide seems to be very satisfactory. Caustic extraction liquors containing considerable portions of sodium sulfide may be used directly in the sulfate cooking process or may be sent to the sulfate recovery system. Consequently, a strong alkali refining process may be advantageously combined with a sulfate pulping operation. If the strong extraction liquors are not utilized in a sulfate operation, the caustic either must be recovered by evaporation and burning of the organic material followed by the causticizing of the carbonate formed in the burning process, or the extraction liquors must be submitted to dialysis as is practiced in recovering caustic in the viscose industry.

Recently, several processes have been suggested involving a dilute

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[31] A. Thiriet (to Papeteries Navarre), U. S. Patent 1,829,378 (Oct. 27, 1931).

caustic extraction at elevated temperatures followed by a strong caustic extraction after the pulp has passed through one or more bleaching operations. It is possible, by this combined caustic treatment, to obtain pulps having an alpha content above 98%, and such pulps are said to be satisfactory for the manufacture of cellulose esters and ethers.

It is well known that when cellulose is treated with strong alkali solutions at relatively high temperatures the mercerizing action is greatly inhibited. Some swelling takes place with strong caustic solutions even at relatively high temperatures, but the amount of swelling is small compared to treatment with solutions of the same strength at normal temperatures. Pulp treated with caustic solutions having concentrations of from 5 to 15% at temperatures ranging from 50 to 80°C. may be successfully used as a paper-making raw material because of the relatively small amount of swelling which has taken place. Under these conditions, pulps of high alpha-cellulose content may be obtained in relatively high yields.

5. Viscosity Control

The manufacturers of cellulose derivatives are accustomed to establishing certain viscosity specifications which the pulp manufacturers must meet and maintain within very narrow limits. The pulp manufacturer has a choice of several methods of maintaining a predetermined viscosity. He may, for example, increase or decrease the severity of the pulping action employed in the production of the unbleached pulp, since by so doing he is able to control the viscosity of the unbleached pulp within certain limits. This practice is frequently followed by changing bleaching conditions with the object of making further changes in the viscosity of the finished product. The final viscosity of a bleached pulp may be lowered considerably by raising the temperature in the final bleaching stage or by operating the final stage in such a way that a considerable excess of hypochlorite remains at the end of the bleaching process. The careful adjustment of *p*H, temperature, and excess hypochlorite enables the pulp manufacturer to control the viscosity of the final product within very narrow limits. It is also possible to lower viscosity by acid treatment at various concentrations and temperatures. The general practice for the regulation of viscosity, however, is usually a combination of control in the cooking process followed by a more precise control in the final stage of the bleaching process.

The foregoing discussion embracing the bleaching and purification of wood cellulose is intended to give a brief historical survey of bleaching and to cover the most modern bleaching procedure developed as a result of many years of research and commercial operation.

I. LITERATURE REVIEWS AND ACKNOWLEDGMENT

Several excellent reviews covering the field of bleaching and pulp purification have appeared in the technical journals; the most important ones have been referred to in the preceding paragraphs. There is no textbook, however, in the English language which covers, in a thorough and complete manner, the entire field of the bleaching and purification of chemical pulps. The reader who is interested in this subject should consult "Die Bleiche des Zellstoffs" by Erich Opfermann and Ernst Hochberger, published by Otto Elsner Verlagsgesellschaft, Berlin, 1935, as part of a series of publications on the technology and practice of papermaking. The section on the bleaching of cellulose is written in two volumes, the first of which is devoted to the preparation and handling of chlorine and hypochlorites as well as a discussion of mill water and its importance in the manufacture and bleaching of cellulose. The second volume deals with the bleaching process itself and covers the historical development of bleaching and equipment together with a large mass of theoretical data. Very complete bibliographies of the particular subjects appear at the end of each chapter. The practice described in these two volumes places considerably more emphasis on European practice than on that in this country which is, of course, to be expected. The author wishes to acknowledge the value of these two volumes as an aid in the preparation of this chapter as well as the assistance of members of the staff of the Research Department of the Pulp Division of the Weyerhaeuser Timber Company.

Chapter VIII

DERIVATIVES OF CELLULOSE

A. KINETICS AND EQUILIBRIA INVOLVED IN CELLULOSE REACTIONS

H. M. SPURLIN

The main features of cellulose reactions in general are treated in Chapter II of this book, and the individual reactions are discussed later in the present chapter. In addition, many points connected with the influence of fiber structure on reactivity will be found in Chapter III. It appears wise to assemble in one section, however, some conclusions concerning the details of the reactions of cellulose or its derivatives in various reaction media. These considerations are most conveniently treated in the order: (1) homogeneous systems, (2) two-phase systems in which the cellulose phase is amorphous, (3) two-phase systems in which the cellulose phase is at least partially crystalline, and (4) a review of some attempts at a mathematical treatment of fiber reactivity.

This section must be considered as an attempt to present a scheme for considering cellulose reactions from a unified viewpoint which will serve to reconcile the many apparently inconsistent experiments and interpretations thereof to be found in the literature. The viewpoint adopted is essentially that of Staudinger,[1] but it has not been possible to select from Staudinger's numerous publications a satisfactory foundation for a short treatment which will fulfill the desired purpose. Therefore, the plan has been adopted of selecting, from the most recent literature, data which support the viewpoint adopted and of developing the subject therefrom, pointing out how apparently conflicting results may be explained. It has not been possible to give a complete treatment, and the examples selected for discussion were chosen because they are of recent date and are still being discussed in the current literature.

1. Homogeneous Systems

A few cases are known in which cellulose or one of its derivatives undergoes reaction in perfectly homogeneous solution. Cases in point are the

[1] H. Staudinger, *Die hochmolekularen organischen Verbindungen*. J. Springer, Berlin, 1932.

etherification of cellulose dissolved in aqueous alkalies (see Section E of this chapter), the hydrolysis of primary to secondary cellulose acetate (see Section C of this chapter), and the substitution of the free hydroxyls in secondary acetates by higher fatty acids or dibasic acid radicals (see Section C of this chapter). At present, enough is known about polymers in general to enable us to understand the course of these reactions quite completely in a qualitative sense, and rapid progress is being made in the quantitative treatment of individual cases.

It is evident that, in a cellulose chain, at least at the start of the reaction, any one of the hundreds of hydroxyls in the chain has a good chance of reacting. Experience with low-molecular-weight compounds in general would indicate that the primary hydroxyls should react, or, at least, should esterify more rapidly than the two kinds of secondary hydroxyls at positions 2 and 3.[2] Very little quantitative information, however, is available concerning the rates of reaction of low-molecular-weight compounds, of structure comparable to cellulose, with etherifying agents or even with acid anhydrides.

In recent work on the tosylation of the free hydroxyls of highly substituted ethylcellulose[3] and cellulose acetate,[4] the rates of reaction were measured with considerable accuracy, and the results are in agreement with the theory of greater reactivity of the primary hydroxyls. The relative rates for positions 2, 3, and 6 were found to be 2.3, 0.07, and 15, respectively, for ethylcellulose, and 2.2, 0.11, and 23 for cellulose acetate. This represents the greatest difference of reactivities so far reported for the various hydroxyl groups of cellulose, although it is possible that tritylation is even more specific for position 6.[5] In line with this, it should also be noted that replacement of tosyl by halogen occurs only at position 6.[3]

In the above work on tosylation, there was no question of interference of a tosyl group in either position 2 or 3 with reaction of the adjoining group, as it was shown that the number of glucose units with both positions 2 and 3 available for substitution was quite small.[3, 6]

However, the very fact that at least one of the secondary positions was already substituted with ethoxyl or acetate suggests that possibly the relatively low reactivity of the secondary hydroxyls indicated by the above

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[2] G. B. Hatch and H. Adkins, *J. Am. Chem. Soc.*, **59**, 1694 (1937).

[3] J. F. Mahoney and C. B. Purves, *J. Am. Chem. Soc.*, **64**, 9 (1942).

[4] T. S. Gardner and C. B. Purves, *J. Am. Chem. Soc.*, **64**, 1539 (1942).

[5] I. Sakurada and T. Kitabatake, *J. Soc. Chem. Ind., Japan*, **37**, suppl. binding, 604 (1934).

[6] F. B. Cramer, R. C. Hockett, and C. B. Purves, *J. Am. Chem. Soc.*, **61**, 3463 (1939).

work might have been due to steric hindrance. If this interpretation is correct, it would be expected that tosylation of cellulose itself dissolved in a quaternary base would lead to more nearly the same rates of tosylation of the primary and secondary hydroxyls. This would bring the tosylation reaction more in accord with the other reactions which have been studied.

In the studies of the reactions of dissolved cellulose, it has been possible to get more complete information about the formation of the cellulose ethers than of cellulose acetate.[3, 7] It was found that cellulose dispersed in quaternary bases reacted with alkylating agents at the primary position with a rate equal to the sum of the rates of the two secondary positions. Under other modes of reaction (*e. g.*, fiber swollen in caustic), the secondary positions reacted more rapidly, with the interesting trend that, as the caustic concentration used for preparation of the products increased, the relative rate of alkylation in the secondary position increased, becoming greater than that in the primary position for two of the products. In addition to the theory of interference with reaction due to hydrogen bonding in position 6, advanced by Mahoney and Purves[3] to explain these findings, there is a possibility that these results may be attributed to a greater acidity of one or both of the secondary hydroxyls, making them especially likely to react at high caustic concentrations.

The results of Cramer and Purves[8] on cellulose acetate lend support to the view that for commercially important reactions the various positions in an unsubstituted or completely substituted glucose unit of cellulose do not differ in reactivity by much more than a ratio of 2:1. The five papers of Purves and his collaborators[3, 4, 6, 7, 8] do contain evidence, however, that substitution in the 2 or 3 position markedly affects the rate of reaction in the adjoining position, the effect in both etherification and hydrolysis of acetate groups having been in such a direction as to make the number of unsubstituted hydroxyls adjoining one another less than would be predicted on the basis of absolutely random reaction.

Another method of attack used with some success in the study of the distributions of substituents along cellulose chains has been to hydrolyze partially substituted cellulose ethers and determine the relative proportions of glucose units with zero, one, two, and three substituents. Most of this work has been done with the purpose of supporting some hypothesis concerning cellulose reactivity, but, as was pointed out by Spurlin,[9] all of the available results, with the exception of a few on the methylation of

[7] J. F. Mahoney and C. B. Purves, *J. Am. Chem. Soc.*, **64**, 15 (1942).
[8] F. B. Cramer and C. B. Purves, *J. Am. Chem. Soc.*, **61**, 3458 (1939).
[9] H. M. Spurlin, *J. Am. Chem. Soc.*, **61**, 2222 (1939).

sodium hydroxide-copper oxide complex compounds of cellulose, are compatible with the concept of almost equal reactivity of all three kinds of hydroxyls and random distribution of the substituents along the chain. As this type of work is concerned almost entirely with cellulose ethers, it is discussed in more detail in Section E of this chapter. It suffices now to point out that hydrolysis of cellulose ethers and determination of the relative amounts of the resulting glucose units with zero, one, two, and three substituents, without determining the relative amounts of the individual substituted glucoses, is a much less powerful tool for studying cellulose reactivity than the methods of Purves and his collaborators reported in the references cited above.

In the same manner that attempts have been made to settle questions of reaction mechanism by isolating the products of complete hydrolysis of cellulose ethers, Lieser[10] has attempted to study the uniformity of substitution of cellulose xanthate by replacing each xanthate group by methyl, subjecting the resulting methylcellulose to acetolysis, and determining the yield of cellobiose octaacetate. He obtained considerable quantities of this substance (10.4% and 11.3% by weight from a methylcellulose of average substitution 0.5, while cellulose under analogous conditions gave 46%), and concluded that this result is not compatible with the concept of uniform availability for substitution of all hydroxyl groups in the cellulose.

Lieser's conclusion does not stand up when examined in the light of the distribution curves for the various types of substituted glucoses under the assumption of uniform reactivity of all hydroxyls. (Lieser accepts this viewpoint in his latest article.[11]) For example, under the assumption of equal reactivity of all hydroxyls, it is found that a methylcellulose of substitution 0.5 will contain unsubstituted glucose units to the extent of 57.8% of the total number of glucose units.[12] The chance that any two adjoining glucose units that happen to be hydrolyzed off together as a cellobiose unit will be unsubstituted is, accordingly, 57.8% of 57.8%, or 33.4%. Correcting for the difference in weight per glucose unit between methylcellulose and cellulose, this chance becomes 32%. Actually, the ratios of the yields obtained from methylcellulose to that from cellulose were only 21% and 25% in the two cases, well below that to be expected from the laws of chance.

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[10] T. Lieser, *Ann.*, **483**, 132 (1930).

[11] T. Lieser, *Kolloid-Z.*, **94**, 96 (1941); also T. Lieser and E. Leckzyck, *Ann.*, **522**, 56 (1936).

[12] Figure 41, Section E of this chapter; the exact formula is $C_0 = (1 - (S/3))^3$, where C_0 equals the proportion of unsubstituted glucose units and S equals the degree of substitution.

It is therefore evident that these results cannot be used to draw conclusions concerning the distribution of substituents in the derivatives under discussion; similar difficulties will undoubtedly be encountered in any further attempts of this type.

Another method of study of the distribution of substituents is to tritylate and assume that the only unsubstituted hydroxyls reacting are those in position 6. This method has been criticized[8] on the basis that tritylation is not selective enough, but the results obtained[5, 13] are in agreement with the conclusion of Purves and Mahoney that about a third of the free hydroxyls in cellulose acetate are in the primary position.

It will be seen that there is a fairly respectable body of evidence showing that there is quite random distribution of substituents along the cellulose chain if all portions of the chain have been equally available for substitution. This conclusion is almost inescapable anyway, as all of the cellulose derivatives form perfectly continuous series with gradually altering properties as the substitution is increased and as no evidence of sudden changes in properties at degrees of substitution of 1 or 2 can be found.

It must be pointed out again, however, that a considerable amount of interference may be expected between groups on positions 2 and 3. Insufficient data are available to evaluate the extent of this interference quantitatively, and it is necessary to go to other fields for information bearing on this point. In the case of polyacrylic acid,[14] it has been shown that the presence of already ionized carboxyl groups in the macromolecule tends to repress the ionization of the remainder to a noticeable degree. The effect in this case (carboxyl groups on neighboring carbons[15]) is slight enough, however, for the titration curve of polyacrylic acid at the point of half neutralization to have a slope only twice that of a monobasic acid. The induction effect of neighboring groups would be expected to be much smaller in the case of nonionic reactions, but steric effects could be larger. The titration curves of polyuronic acids also do not differ noticeably from those of monobasic acids.[16] In this case, the carboxyl groups are in different units of the polymer chain, and it may be concluded from this that the state of reaction of one unit of a polysaccharide is without influence on the state of reaction of its neighbors. With the exception of possible interference between positions 2 and 3 of the same glucose unit, therefore, the use of the

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[13] P. P. Shorygin, A. E. Veĭtsman, and N. N. Makarova-Zemlyanskaya, *J. Gen. Chem. U.S.S.R.*, **7**, 430 (1937).

[14] W. Kern, *Z. physik. Chem.*, **A181**, 249 (1938).

[15] C. S. Marvel, J. H. Sample, and M. F. Roy, *J. Am. Chem. Soc.*, **61**, 3244 (1939).

[16] A. M. Sookne and M. Harris, *J. Research Natl. Bur. Standards*, **25**, 47 (1940).

concept of random or permutoid reaction in the subsequent portions of this section seems justified. By this it is not meant that the three kinds of hydroxyls will have the same reactivity, but that each has a certain relative chance of reaction which is independent of the degree of substitution of the rest of the chain and, therefore, is susceptible of ready mathematical treatment. As pointed out above, the three kinds of hydroxyls may in some cases differ in reactivity by as much as 200:1, but more commonly by not as much as 10:1.

2. Cellulose as a Separate, Amorphous Phase

As will be shown in Chapter IX, when either cellulose or its derivatives are precipitated from solution, they generally form a second phase which is, from the thermodynamic point of view, essentially a liquid. This precipitated phase will be more or less viscous, depending on conditions, but it is usually in quite good equilibrium with the supernatant liquid, especially if the precipitation is carried out slowly and with good agitation. From what has been said above, it follows that the principle of random reaction of the individual glucose units of the cellulose chain will apply to this case; also, the concentration of reagents in the cellulose phase will be governed by the usual laws of distribution of a substance between two phases in equilibrium with each other.

This case merits discussion because numerous efforts have been made to investigate the nature of cellulose derivatives such as the cuprammonium complex and the xanthate by precipitating them from solution, and too often the assumption has been made that the state of substitution of the cellulose chain is not altered by this procedure. Yet, it is known that in the case of both cuprammonium complex and xanthate the degree of substitution is a function of the concentration of the medium. With cuprammonium complex in solution, the equilibrium is very rapidly established; precipitation occurs immediately when the solution is diluted or when the *p*H is changed beyond a certain limit. These conclusions are based on the recent work of Jolley[17] which has clarified the nature of cuprammine solutions. This subject is discussed more fully in Section D of this chapter.

A complication occurs in the case of cuprammonium solutions due to the fact that a great excess of ammonia is needed to keep the copper in solution; dilution causes precipitation of $Cu(OH)_2$. This inherent instability of the copper complex must extend to the precipitated phase, and long-

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[17] L. J. Jolley, *J. Textile Inst.*, **30**, T4, T22 (1939).

continued washing with a solvent for ammonia will therefore cause precipitation of copper as oxide or hydroxide. Hence, the results of Lieser,[18] which showed that, on precipitation and prolonged washing of cuprammonium solutions with methanol, the final solid had a ratio of Cu: $C_6H_{10}O_5$ corresponding to complete reaction of only half of the $C_6H_{10}O_5$ groups, may be fully explained as follows on the basis of complete, macromolecular reaction of the cellulose.

First, as shown by Jolley,[17] the extent of reaction of copper with the cellulose is a function of the composition of the solution, dilution with respect to copper causing the ratio of combined Cu: $C_6H_{10}O_5$ to fall. (This behavior is demanded by the considerations advanced earlier in this section, if precipitation of the cellulose is to occur at all on dilution.) When the ratio falls below 0.8, the longer cellulose chains become insoluble; by the time this ratio reaches 0.5, the cellulose has become entirely insoluble. Between these two points two coexisting phases are present; the precipitated phase consists chiefly of the higher-molecular-weight material. The precipitate is found by experiment to contain less bound copper than the dissolved portion (the calculation in the case of the precipitate is rendered uncertain by the influence of the unknown amount of bound water and the Donnan effect). That this must be the case is indicated by the fact that precipitation occurs because of some type of interaction between the chains which is opposed by the bound copper; application of thermodynamic principles shows that, if the chains are altered in environment in such a manner as to increase the extent of this interaction which is opposed by combination with the copper, the extent of combination with the copper will tend to decline. Experimentally, then, in an aqueous medium, precipitation does not occur until the extent of combination with copper has dropped much below the maximum realizable. The same type of behavior must be encountered when methanol is the precipitating agent, and the precipitated phase must have less than the maximum degree of reaction with copper possible in the solution.

Further, on washing the precipitate with methanol, additional quantities of copper must have been removed as long as ammonia remained to form the cuprammonium complex. Therefore, the final copper-cellulose ratio in nowise reflects that existing in the solution, and all arguments concerning the degree of dispersion of cellulose in cuprammonium based thereon lose their validity.

Most of the points mentioned in the above treatment of the cupram-

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[18] T. Lieser, *Ann.*, **528**, 276 (1937).

monium problem were referred to in the discussion[19] which followed the presentation of a paper by Lieser before the German Society of Wood and Paper Chemists and Engineers.

Conditions with respect to the determination of the extent of reaction in cellulose xanthates are, fortunately, not quite as difficult to deal with. The xanthate is a fairly stable derivative, with a measurably slow rate of dissociation at 0°C., and by working quickly it should be possible to precipitate the compound existing in solution and to determine the ratio of combined xanthate groups to cellulose. It must be remembered, however, that the xanthate groups can wander from one cellulose chain to another[20, 21] in the presence of alkali and, therefore, presumably can wander from one alcohol to another. Possibly, therefore, on washing with methanol in the presence of caustic there is more removal of the xanthate group than is the case with cold ammonium chloride solutions, and the discrepancy between the claims of Lieser[18, 22] and Bredée[21] concerning the state of reaction in fibrous xanthate may thus be explained. In fact, Lieser[23] in a recent publication accepts the experimental findings of Bredée without admitting the universal validity of the arguments advanced in this section concerning the state in solution of a compound such as the cuprammonium complex.

It is evident that precipitation is not a suitable tool for determining the nature of labile compounds of cellulose in solution, and, when used with moderately unstable compounds, the suitability of the precipitation methods used should be checked by suitable control experiments. For example, in the case cited above of xanthate and methanol, it would be necessary to investigate the action of alkaline methanol on the precipitated xanthate. It is not sufficient to try the precipitation method on analogous low-molecular-weight compounds, as these will yield a precipitate of stoichiometric composition even if dissociation in solution is extensive, as is evident from the application of the phase rule. Contrasted with this, a polymer precipitate will exhibit a degree of reaction continuously variable with the composition of the supernatant liquid, in the same manner as ion-exchange substances.

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[19] *Angew. Chem.*, **54**, 134 (1941).

[20] G. Centola, *Atti X Congr. Internatl. Chim. Roma, 1938*. Vol. IV, pp. 117, 129, 138, 722, 728; cited by Bredée.[21]

[21] H. L. Bredée, *Kolloid-Z.*, **94**, 81 (1941).

[22] T. Lieser, *Ann.*, **464**, 43 (1928); **470**, 104 (1929); **483**, 132 (1930).

[23] T. Lieser, *Ber.*, **74**, 708 (1941).

3. Cellulose Partially Crystalline

(a) *Reaction of Amorphous Portion*

Almost all cellulose reactions start with fibrous cellulose, which is, as was shown in Chapter III, usually partially crystalline and partially non-crystalline. As is emphasized repeatedly throughout this book, the chief problem in cellulose derivative preparation is to make all portions of the cellulose fiber available for reaction. This has been shown to be possible only if the fiber structure is highly swollen before or during the reaction. There is not much in a general way which needs to be said at this point about the details of swelling, individual cases being treated under the respective derivatives and in Chapters III and IX. The overwhelming importance of swelling in all technically important cellulose reactions should not be overlooked because of the relatively short treatment given here.

Swelling acts to loosen the intermicellar structure of cellulose, converting it to a state closely approximating solution; indeed, long portions of the cellulose chains are free to move about in the swelling liquid, which is taken up into the structure due to the free energy of dilution of the mobile segments of the cellulose chains (see Chapter IX, A and B). In case complex formation with ions is involved, the osmotic pressure of the counter ions and electrostatic repulsion between the chains, modified by the Donnan effect if salts are present, contribute powerfully to the forces favoring swelling. More precisely stated, there is a certain average equilibrium distribution curve for the distance of the counter ions from the cellulose chain, determined by the nature of the ions in solution; if the counter ions are constrained to an average position closer to the chain, there is created a repulsive force between chains.

In addition, of course, there is an increase of volume due to the actual space required for the groups which are firmly attached to the cellulose chain and which promote swelling by reducing the degree of hydrogen bonding or the area of contact between chains (see Chapter IX). It must be realized, however, that this mere increase of volume will only promote reactivity insofar as the presence of the large solvating groups allows channels to be formed big enough to allow reagents to penetrate the cellulose structure. Far more important is the actual intake of free liquid into the structure mentioned above, which converts the intermicellar region to a condition approximating the state of a gelatin or agar jelly. As is well known, the presence of the long-chain molecules and the very high viscosity of these jellies do not prevent the rate of diffusion of even moderately

large molecules through the jelly structure from being almost as rapid as through water.[24, 25]

Due, then, to the imbibition of liquid, the penetration of reagents into the intermicellar region may be made quite rapid. Any crystalline region remaining in the swollen fiber cannot be as available for reaction. It is thus obvious that reaction will always proceed more rapidly in the intermicellar region than in the crystalline region.

This viewpoint is universally accepted, and differences of opinion concerning cellulose reactivity center about the question whether, in a particular case, some mechanism is operating which will enable the crystalline material to react eventually to the same extent as the intermicellar material. This will, in general, be possible only if one of three conditions is fulfilled: (1) the reaction goes to completion, all of the glucose units becoming trisubstituted (or monosubstituted if a reaction is found specific to a particular hydroxyl); (2) an equilibrium is set up, the extent of reaction being determined by the concentration of the reagents; or (3) the fiber passes into solution and all differentiation between amorphous and crystalline regions is lost.

The first and third of these conditions are used in the preparation of uniform organic esters of substitution less than 3, a completely substituted and therefore uniform product being subjected to partial hydrolysis in solution, where equal availability of all chains is assured. Nitrocellulose may be obtained uniform because in its preparation an equilibrium is reached (see Section B of this chapter). Cellulose ethers prepared in the fibrous state are notoriously nonuniform,[7] while those which pass into solution during preparation, such as the commercially important product of substitution over 2 and the lower-substitution products prepared from cellulose dissolved in organic bases, are quite uniform.

There is little doubt concerning the essential uniformity of derivatives such as those named, due to their occurrence in series of gradually increasing substitution without sharp breaks in properties at any integral value of substitution. Also, their behavior on fractionation leads to separation of higher-molecular-weight portions from lower, but results in very little difference of substitution in the various fractions as mentioned previously. However, there has been much discussion about the state of reaction of such products as the xanthate and copper-containing complexes, which, as was shown above, are too unstable to withstand isolation and study without fear of at least partial decomposition.

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[24] R. Taft and L. E. Malm, *J. Phys. Chem.*, **43**, 499 (1939).

[25] J. J. Bikerman, *J. Phys. Chem.*, **46**, 724 (1942).

Much of the misunderstanding about these products has been caused by indiscriminate use of methods based on the phase rule which have valid application only to cases where a solid, crystalline phase of invariant composition is present. Little difficulty has been experienced in explaining cases of mixed crystals with limited or unlimited miscibility when encountered with low-molecular-weight compounds, but so far there have been very few attempts to apply these principles to the very similar case of cellulose. It is generally accepted that the cellulose micelle is at best a very imperfect crystal, due to the random distribution of chain ends and various types of distortion. The fact that the crystal can exist with a wide range of content of these imperfections demonstrates that it will have a certain tolerance for other types of imperfections. Thus, if alkali cellulose is in equilibrium with caustic of a given concentration, there will be a certain well-defined tendency for any given pair of sodium and hydroxide ions to leave the crystal lattice and go into the solution. The same will apply to the water molecules also present in the crystal lattice. When any individual molecule or pair of ions leaves the crystal structure, there is no violent change of stability; there will be a continuous curve of escaping tendency of sodium and hydroxide ions, for example, which will cause their concentration in an individual micelle to vary with caustic concentration. This micelle will not lose its crystalline identity until its composition has altered to the point that some other crystal form becomes more stable, or the crystal structure is lost altogether, or the substance dissolves. The case is thus entirely analogous from a mathematical standpoint to a system forming mixed crystals of limited miscibility, the extent of mixed crystal formation being a function of the degree of instability introduced into the lattice by the substitution of one type of structure for another at a given point.

The existence of a crystalline addition compound exerts a definite stabilizing action with respect to a certain composition, of course, and a considerable tendency may be expected for flattening out of the curve relating composition of the cellulose phase to the composition of the bath with which it is in equilibrium around compositions corresponding to the stoichiometric addition compound. In the particular case of cellulose fibers, however, it must be remembered that only a portion of the structure is crystalline and that the remainder will react in a permutoid manner, its composition following a curve resembling the titration curve of a weak acid as the concentration of reagent is varied.[26]

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[26] S. M. Neale, *J. Textile Inst.*, 22, T320 (1931).

There is the further complication that the crystalline regions in cellulose fibers are subjected to physical constraints which alter the tendency of one crystal form to change into another, and cause the size of the crystallites to vary with the degree of substitution.[27] As a consequence of the fact that these constraints are not the same for all crystallites, it is possible for two kinds of crystalline structure to coexist over a range of reagent compositions (see Chapter III, A).

The three factors mentioned—mixed crystal-type structure, presence of amorphous material, and physical constraints in the crystallites—make it difficult to draw conclusions as to the composition of the crystalline phase from absorption curves, such as those discussed in Section D of this chapter. It is likely that the conclusions of Saito[28] are more valid than those of other workers who have entirely neglected the possibility that water enters into the crystal structure of alkali cellulose. Of course, the conclusions of Neale[26] to the effect that the amorphous region will contain large quantities of caustic due to the operation of the Donnan effect are entirely valid, and would have to be taken into account in any earnest attempt to derive the composition of the crystalline portion of the alkali cellulose fiber from phase-rule studies.

That the question of the composition of the crystalline portion of alkali cellulose is of more than academic interest is shown by one phase of the polemic between Bredée[21] on one side, and Lieser[29] and Schramek[30] on the other. Bredee was attempting to show that reaction between gaseous CS_2 and alkali cellulose occurred at least partially in the crystalline phase by making a caustic balance and showing that there was not enough NaOH in the intermicellar region to account for all of the reaction that had occurred. In order to do this, Bredée had to assume that the crystalline region had one NaOH per $C_6H_{10}O_5$,[31] an opinion which is supported by the work of Neale and Saito. The assumption that this NaOH will cause xanthation to occur at exactly the place where the NaOH occurred in the crystal lattice is, on the other hand, not justified. It is possible, however, to reconcile the facts presented by the above authors on this question which is so important for the whole understanding of cellulose reaction and solution.

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[27] For a discussion of the manner in which this comes about, see T. Alfrey and H. Mark, *J. Phys. Chem.*, **46**, 112 (1942).

[28] G. Saito, *J. Soc. Chem. Ind., Japan*, **43**, B133 (1940).

[29] T. Lieser, *Kolloid-Z.*, **94**, 96 (1941).

[30] W. Schramek, *Kolloid-Z.*, **94**, 93 (1941).

[31] K. Hess, C. Trogus, and O. Schwarzkopf, *Z. physik. Chem.*, **A162**, 187 (1932).

First, as pointed out above, the intermicellar material must react first. This will result in an exhaustion of the NaOH in this neighborhood, and thus in the migration of NaOH out of the crystal lattice at the same time that reaction proceeds on the surface of the crystallite. This NaOH moving out will meet CS_2 moving in, causing further reaction to occur in the intermicellar region. As it is known that the loss of alkali from alkali cellulose is very rapid and it may be assumed that xanthation is slower, the

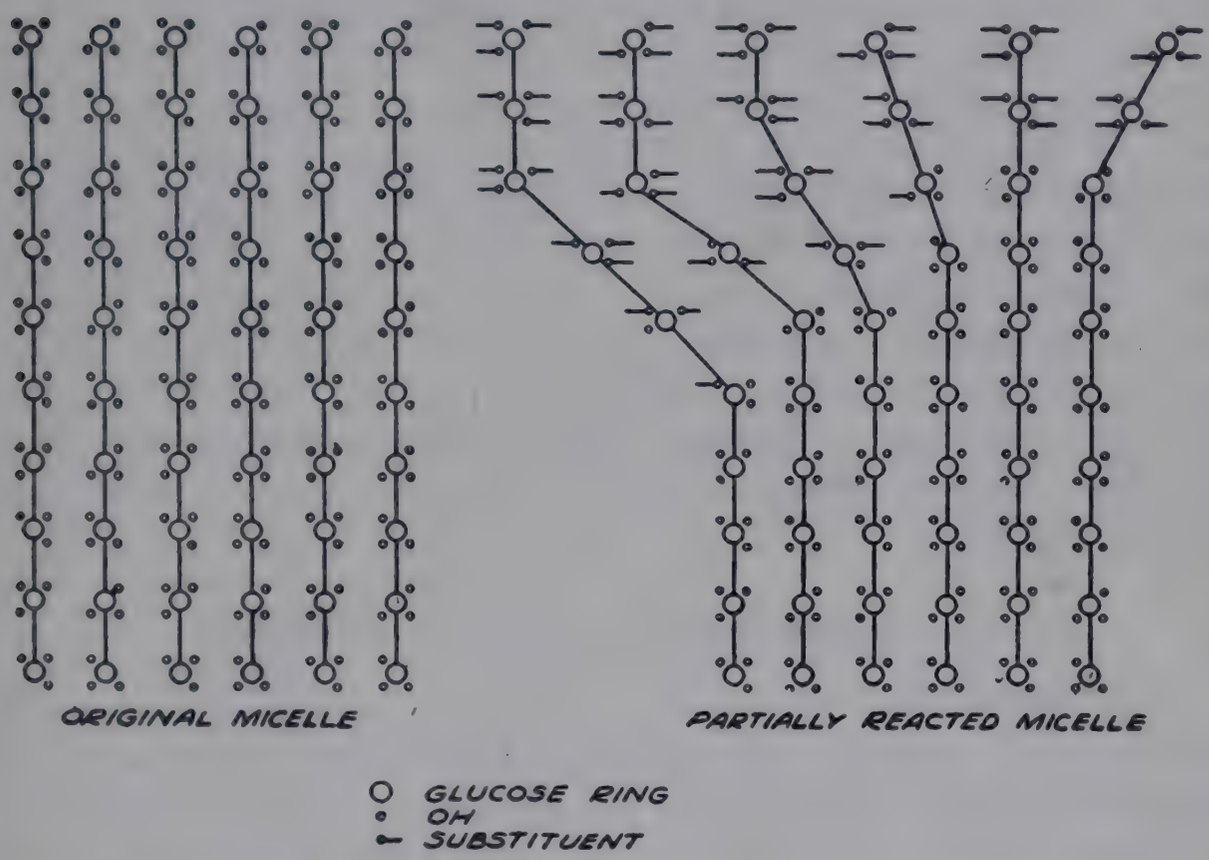

FIG. 1.—REACTION OF CELLULOSE MICELLE WITH RETENTION OF FIBER STRUCTURE (SPURLIN[32]).

Comparison of unreacted micelle with partially reacted micelle, the reaction proceeding from one corner.

net result will be very extensive reaction in the intermicellar region and limited reaction in the crystalline region. At the first stage of the reaction (3 hrs.) alkali cellulose x-ray interferences are still present, but they disappear in 36 hrs.[20] This may show simply that the NaOH has all diffused out of the crystallite, but in this case hydrate cellulose lines should appear. It is therefore more logical to assume that enough xanthation has occurred throughout the crystallite to destroy the crystal structure.

[32] H. M. Spurlin, *Trans. Electrochem. Soc.*, **73**, 95 (1938).

This does not mean that a perfectly uniform product has been obtained by this time. It is, however, fairly certain that dilute solutions of xanthate may be obtained in the monodispersed state,[33] and we must assume a constant tendency for even commercial viscose to approach this state during the time of decreasing viscosity (see Section F of this chapter).

(*b*) *Reaction of Crystalline Portion*

The above paragraphs have merely pointed out the much greater reactivity of the uncrystallized portion of the fiber without attempting to account for the fact that the crystalline portion does eventually react in most cases, and that it frequently reacts without losing the crystal structure. A likely assumption is that the first stages of the reaction of the outer layers of the crystallite result in a loosening of the adjoining structure which permits this to swell in the same manner as the intermicellar material. Thus, it is possible to picture (Fig. 1[32]) a zone of unreacted crystal holding the structure together; a zone of disordered, swollen structure; and a zone where reaction is complete and recrystallization has occurred with the chains held in the same relative positions as before reaction had occurred. As reaction proceeds, this zone continues to grow, preserving the crystalline entity.

4. Mathematical Treatment of Reactivity

Many efforts have been made to set up a generalized mathematical treatment of reactivity. The following short summary of these efforts is appended for those interested in this question. Since the reactivity of cellulose and its derivatives is so profoundly influenced by the degree of swelling, any simple mathematical treatment based on structural considerations is unlikely to be of much utility.

The two factors which have been regarded as the limiting ones in reaction rate studies are diffusion and chemical reactivity. For example, for nitrocellulose preparation, Atsuki and Ishiwara[34] found the following equations to hold:

$$\text{Diffusion: } (a - n) = ae^{-0.649t^{1/2}}$$

$$\text{Nitration: } 0.0291 = \frac{(1 - \sqrt{1 - m})^2}{2t}$$

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[33] H. Staudinger and F. Zapf, *J. prakt. Chem.*, **156**, 261 (1940).

[34] K. Atsuki and M. Ishiwara, *Proc. Imp. Acad.* (Tokyo), **4**, 382 (1928); *Chem. Abstracts*, **22**, 4792 (1928).

Diffusion to the center of the fiber was complete in 25 minutes, while nitration was complete in 100 minutes, so the two factors were of approximately equal importance.

In general, however, the diffusion factor has been neglected. The most-used equation for esterification rates is the following:

$$x = kt^b$$

Originally derived for acetylation without catalysts,[35] it has been used for nitration[36, 37] and benzoylation,[38] and has been modified to apply to catalyzed acetylations[39] by modifying k:

$$k = pc^{1/q}$$

In connection with these studies on the effect of catalysts on acetylations, Sakurada[39] found that perchloric acid was ten times as powerful as was sulfuric acid.

Nomenclature

a = % total nitrogen in most nitrated product
t = time
n = % total nitrogen in product after time t
m = fraction nitrated in t minutes
x = number of substituted hydroxyl groups per 100 glucose units
k, b, p, q = constants
c = concentration of catalyst

[35] I. Sakurada, *J. Soc. Chem. Ind., Japan*, **35**, B123, B283 (1932); **36**, B280, B299 (1933).

[36] I. Sakurada and M. Shojino, *J. Soc. Chem. Ind., Japan*, **35**, B287 (1932).

[37] T. Nakashima, H. Nakahara, and I. Sakurada, *J. Soc. Chem. Ind., Japan*, **39**, B51 (1936).

[38] A. L. Bernoulli, M. Schenk, and F. Rohner, *Helv. Chim. Acta*, **17**, 897 (1934).

[39] I. Sakurada and M. Miyagute, *J. Soc. Chem. Ind., Japan*, **39**, B91 (1936).

B. INORGANIC ESTERS

J. Barsha

1. Nitrocellulose[1]

Nitrocellulose, the only inorganic ester of cellulose which has attained commercial importance, is also the oldest cellulose derivative. Braconnot in 1832 and Pelouze in 1838 had nitrated various materials including starch, wood fiber, cotton, and paper with concentrated nitric acid. However, in 1845, Schönbein nitrated cellulose with a mixture of nitric and sulfuric acids, and he is generally credited with the discovery of nitrocellulose. The early history of nitrocellulose is associated largely with the attempts to manufacture it for military explosives. It was not until about 1866, when Abel showed that the stability of nitrocellulose is improved enormously by pulping the nitrated fibers in a paper beater and then washing out the retained acid, that the manufacture of nitrocellulose was established on a sound basis. The next major step in the history of nitrocellulose was the development of celluloid, the first synthetic plastic. This was followed by the development of the nitrocellulose lacquer industry, which experienced its great expansion in the years following World War I.

(*a*) *Preparation of Nitrocellulose*

Sources of Cellulose for Nitration. Cotton, the purest form in which cellulose occurs abundantly in nature, has been used in various forms as the chief source of cellulose for the manufacture of nitrocellulose. In the early days, the cotton was used in the form of skeins, rovings, or waste; this was later followed by the use of cotton linters. The advantages of linters over staple cotton in nitrocellulose manufacture include: (a) lower cost, (b) greater ease of handling and manipulation in the plant,

[1] A detailed account of the early history of nitrocellulose and a bibliography of all the literature up to 1920 are given by E. C. Worden, *Technology of Cellulose Esters*. Vol. 1, E. C. Worden, Millburn, N. J., 1921. Patent literature has been systematically compiled by O. Faust, *Celluloseverbindungen und besonders wichtige Verwendungsgebiete*. J. Springer, Berlin, 1935.

and (c) less pulping required in purification of the smokeless powder grade of nitrocellulose.

Efforts have not been lacking to find sources of cellulose other than cotton,[2] especially in war time when the demand for nitrocellulose for use in smokeless powder is very great.[3] While these efforts have been directed largely toward the development of wood pulp[4] suitable for nitration, attention has also been given to the preparation of cellulose from other plants.[5, 6] In 1912, Tedesco obtained results which led him to believe that nitrocellulose from wood pulp is much less stable than nitrocellulose from cotton.[7] However, investigations by Nitzelnadel[8] and also by Schwalbe and Schrimpff[9] showed that satisfactorily stable nitrocellulose for smokeless powder can be made from wood pulp. During World War I, large quantities of wood pulp (usually in the form of creped tissue paper) were nitrated in Germany. During the same period of scarcity of cotton, the nitrocellulose industry in the United States went from mill-run linters to second-cut linters and later to hull fiber. Large-scale attempts in this country in 1918 to nitrate crepe paper encountered the following difficulties: (a) the product tended to gelatinize during nitration, (b) the quantity of acid retained after wringing was high, (c) the yield of nitrocellulose was only about 1.2 pounds per pound of wood pulp as compared with 1.5 pounds from cotton, (d) dehydration of the nitrated pulp with alcohol was slower because of the finely divided nature of the product. Cellulose with physical form suitable for nitration was finally obtained with a mixture of equal parts of wood pulp and cotton linters. The nitrocellulose produced from this mixture had satisfactory stability.[10]

Considerable progress has been made in the last twenty or thirty years in the development of methods for manufacturing well-purified pulps for chemical purposes and for putting wood pulp into suitable physical form for nitration. The developments in this field by the Brown Company

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[2] F. Olsen, *Ind. Eng. Chem.*, **21**, 354 (1929).

[3] A. D. Styles, *Chem. & Met. Eng.*, **48**, No. 12, 80 (1941).

[4] W. Scharrnbeck, *Z. ges. Schiess- u. Sprengstoffw.*, **29**, 33, 67, 98, 133, 196, 230, 266 (1934).

[5] P. Demougin, *Mém. poudres*, **23**, 268 (1928).

[6] E. Afferni and C. Milani, *Ann. chim. applicata*, **30**, 248 (1940).

[7] H. Tedesco, *Z. ges. Schiess- u. Sprengstoffw.*, **7**, 474 (1912).

[8] K. A. Nitzelnadel, *Z. ges. Schiess- u. Sprengstoffw.*, **7**, 257, 301, 339, 384, 409 (1912).

[9] C. G. Schwalbe and A. Schrimpff, *Z. angew. Chem.*, **27**, 662 (1914); A. Schrimpff, *Nitrocellulose aus Baumwolle und Holzzellstoffen*. J. F. Lehmann, Munich, 1919.

[10] R. G. Woodbridge, Jr., *Ind Eng. Chem.*, **12**, 380 (1920).

have been described in detail by Schur and Hoos.[11] They found that if purified pulp is shredded in the presence of about its own weight of water and then redried, the shredded pulp can be nitrated by the same method that is used in the commercial nitration of linters. They also reported that customary nitrating equipment and mixed acid gave good results with purified wood pulp in the form of light-weight paper (tissue). Pulpboard cut into small pieces can be satisfactorily nitrated in the usual equipment if the nitrating acid is made unusually rich in nitric acid.

The most successful process in the United States for preparing wood pulp for nitration was developed by Stern and has been in full commercial operation for several years.[12] In this process, wood pulp sheets are shredded "by shearing in one direction with reference to the sheet, splitting in a direction transverse to the shearing, and tearing at the ends." The shredded pulp can be nitrated satisfactorily in the usual equipment and by essentially the same procedure as is used for linters.

Mention should also be made of the use of a moderate amount of regenerated cellulose film (scrap cellophane) in the manufacture of one grade of nitrocellulose for lacquers.[13]

Nitration with HNO_3—H_2SO_4—H_2O. Although nitric acid itself in both liquid and vapor form and also mixtures of nitric acid with a wide variety of other chemicals have been used experimentally to nitrate cellulose, the nitrocellulose industry still employs HNO_3—H_2SO_4—H_2O mixtures such as have been used for this purpose for almost a century. In other reactions of cellulose which are carried out on a large scale today, such as the preparation of viscose, cellulose acetate, and ethylcellulose, the cellulose dissolves and its original fibrous structure is completely lost. In contrast to these, the nitration of cellulose is effected with complete retention of the original fiber structure, and the chief superficial changes that occur are an increase in the hardness of the fiber and, in the case of cotton, an untwisting of the convoluted fiber.

The extent or degree of nitration of cellulose is most commonly designated by the nitrogen content expressed as per cent nitrogen or, less frequently, as the number of cc. of NO (at 0°C. and 760 mm. pressure) evolved from 1 g. of nitrocellulose. Although it is possible to prepare nitrocellu-

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[11] M. O. Schur and B. G. Hoos, *Ind. Eng. Chem.*, 29, 26 (1937); this reference lists the various patents obtained by the Brown Company and also gives a good summary of other references on the preparation of wood pulp for nitration.

[12] R. L. Stern (to Hercules Powder Co.), U. S. Patent 2,028,080 (Jan. 14, 1936).

[13] P. B. Cochran, M. V. Hitt, and L. V. Taylor, U. S. Patents 1,997,766 (Apr. 16, 1935); 2,150,205 (Mar. 14, 1939).

loses covering the entire range of nitrogen content, the products normally manufactured fall in the broad range of 10–14% N, as shown in Table 1.

Since (as will be discussed later) cellulose nitration is an equilibrium reaction, the extent of nitration at equilibrium is governed primarily by the composition of the mixed acid. The extent of nitration is affected to a lesser degree by the ratio of mixed acid to cellulose, the final nitrogen content being increased, within limits, by an increase in the ratio.[14] The effect of mixed acid composition on the extent of nitration was studied in great detail by Lunge and coworkers.[15, 16, 17] In one of their first series of

TABLE 1

GENERAL TYPES OF MANUFACTURED NITROCELLULOSE

Nitrogen content, %	Field of application	Common active solvents
10.7–11.2	Celluloid plastics, lacquers	Ethyl alcohol
11.2–11.7	Film, lacquers	Ether-alcohol; methanol; ethyl, butyl, and amyl acetates; acetone; methyl ethyl ketone
11.8–12.3	Film, lacquers, rayon, coated fabrics, cements	Ether-alcohol; methanol; ethyl, butyl, and amyl acetates; acetone; methyl ethyl ketone
12.5–13.5	Smokeless powder	Acetone

experiments (Table 2) they attempted to prepare nitrocellulose with nitrogen content as close as possible to the theoretical maximum of 14.14%. Nearly all of the products they obtained fell in the range of 13.5 to 13.8% N even though some of their acid mixtures contained as much as 12.5% water. In other experiments (Table 3) the ratio of H_2SO_4 to HNO_3 was kept nearly constant at slightly less than one while the proportion of water was varied; it was found that the nitrogen content of the nitrocellulose decreases regularly with increase in the proportion of water in the mixed acid. Experiments on the effect of the H_2SO_4:HNO_3 ratio on the course of nitration showed that the rate of nitration decreases rapidly with increase in the above ratio. Maximum nitrogen content was obtained with ratios between 0.25:1 and 3:1. With ratios above 8:1, the product always contains some unnitrated cellulose and the fiber structure is attacked.

[14] J. O. Small and C. A. Higgins, *Chemical Age*, **28**, 211 (1920).

[15] G. Lunge and E. Weintraub, *Z. angew. Chem.*, **12**, 441, 467 (1899).

[16] G. Lunge and J. Bebié, *Z. angew. Chem.*, **14**, 483, 507, 537, 561 (1901).

[17] G. Lunge, *J. Am. Chem. Soc.*, **23**, 527 (1901); this article is a summary of refs. 15 and 16 above.

TABLE 2

EFFECT OF MIXED ACID COMPOSITION ON ATTAINMENT OF MAXIMUM NITRATION OF CELLULOSE (LUNGE AND COWORKERS[17])

Composition of mixed acid			Nitrogen in nitrocellulose, %
H_2SO_4, %	HNO_3, %	H_2O, %	
60.00	27.43	12.57	13.62
62.10	25.79	12.11	13.75
62.95	24.95	12.10	13.83
63.72	25.31	10.97	13.75
64.56	24.65	10.79	13.71
68.02	25.28	5.70	13.76
64.55	26.55	8.88	13.72
63.35	25.31	11.34	13.92
75.33	22.80	1.87	13.53
74.16	22.12	3.72	13.51
72.97	21.63	5.40	13.57
69.90	20.45	9.65	13.64
68.31	20.49	11.20	13.61
67.43	19.37	13.20	13.25
67.32	32.53	0.15	13.62
65.41	31.34	3.25	13.57
63.75	30.80	5.45	13.63
70.68	29.31	10.01	13.68

TABLE 3

EFFECT OF WATER CONTENT OF MIXED ACID ON THE DEGREE OF NITRATION OF CELLULOSE (LUNGE AND COWORKERS[17])

Composition of mixed acid			Nitrogen in nitrocellulose, %	Solubility in ether-alcohol, %
H_2SO_4, %	HNO_3, %	H_2O, %		
45.31	49.07	5.62	13.65	1.50
42.61	46.01	11.38	13.21	5.40
41.03	44.45	14.52	12.76	22.00
40.66	43.85	15.49	12.58	60.00
40.14	43.25	16.61	12.31	99.14
39.45	42.73	17.82	12.05	99.84
38.95	42.15	18.90	11.59	100.02
38.43	41.31	20.26	10.93	99.82
37.20	40.30	22.50	9.76	74.22
36.72	39.78	23.50	9.31	1.15
35.87	38.83	25.30	8.40	0.61
34.41	37.17	28.42	6.50	1.73

Berl, Andress, and Escales[18] studied critically the literature on experimental nitrations with different mixed acids and found good agreement between the results of Lunge and coworkers,[15, 16, 17] Boltenstern,[19] and Demougin.[20] Since the final nitrogen content is determined by the

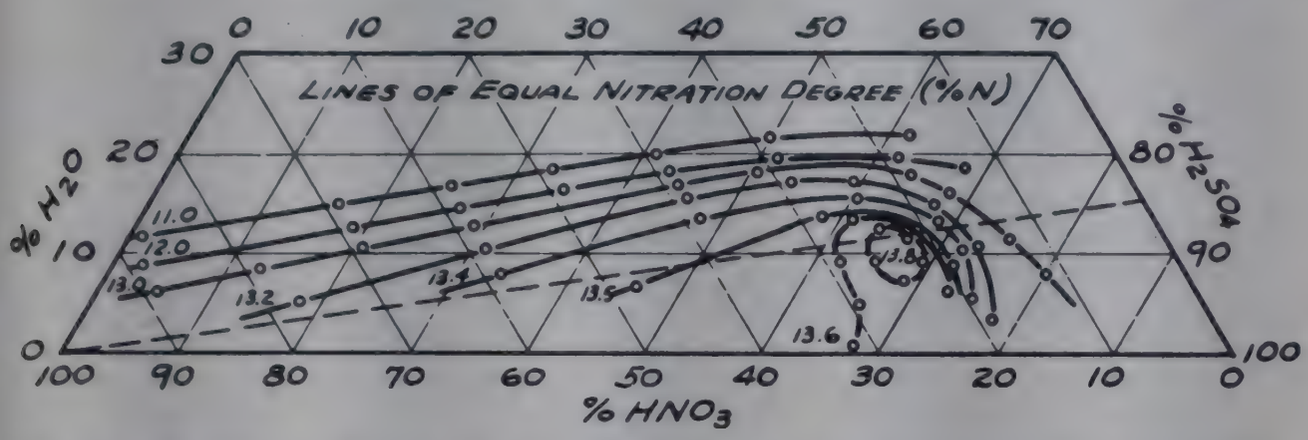

FIG. 2.—EFFECT OF SPENT ACID COMPOSITION ON THE NITROGEN CONTENT OF NITROCELLULOSE (BERL, ANDRESS, AND ESCALES[18]).

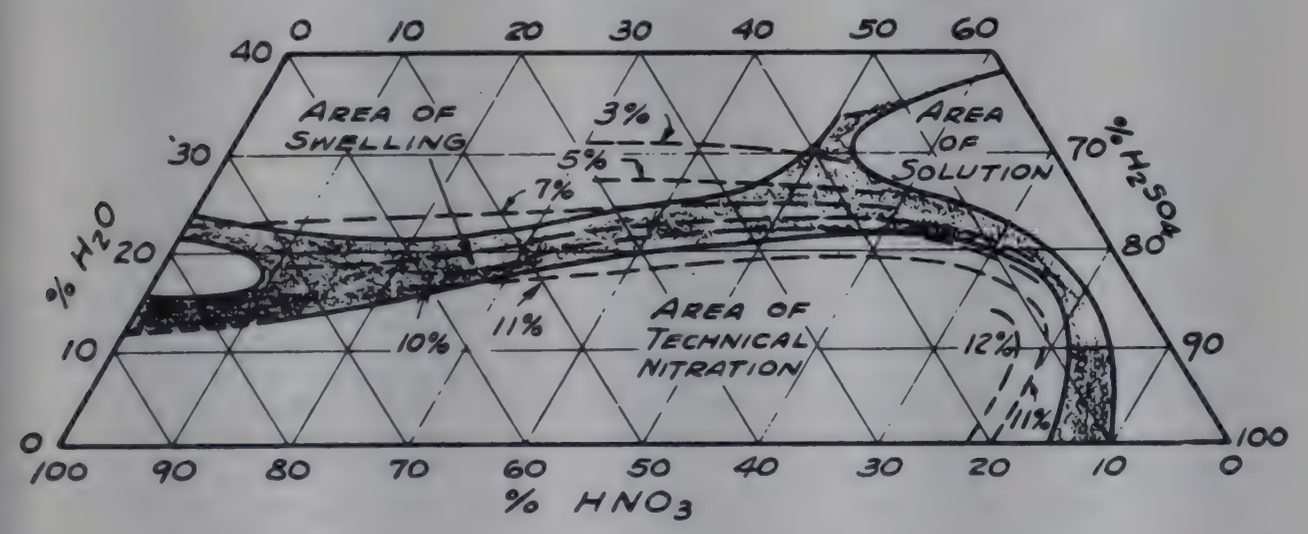

FIG. 3.—EFFECT OF DIPPING ACID COMPOSITION ON THE NITROGEN CONTENT OF NITROCELLULOSE (MILES AND MILBOURN[21]).

composition of the spent acid in contact with the nitrocellulose rather than by that of the original dipping acid, Berl and coworkers calculated the composition of the spent acids from the composition of the dipping acids by the graphical methods of Demougin[20] in cases where only the latter values were given. They then prepared a triangular coordinate diagram

[18] E. Berl, K. R. Andress, and E. Escales, *Beiträge zur Kenntnis der Mischsäure*. J. F. Lehmann, Munich, 1937, p. 32.

[19] W. von Boltenstern, Dissertation, Darmstadt, 1921, p. 86.

[20] P. Demougin, *Mém. poudres*, **23**, 262 (1928).

[21] F. D. Miles and M. Milbourn. *J. Phys. Chem.*, **34**, 2598 (1930).

of the spent acid compositions in which lines were drawn connecting compositions which produced the same nitrogen content (see Fig. 2). Miles and Milbourn[21] have drawn a somewhat similar diagram in which the compositions shown are those of the dipping acids (see Fig. 3).

Despite the wide variety of HNO_3—H_2SO_4—H_2O compositions shown in Figure 2 which can yield nitrocellulose of a given nitrogen content, the selection for industrial nitrations is fairly limited by considerations of cost

TABLE 4

COMPOSITION OF COMMERCIAL NITRATING ACIDS AND THE NITROGEN CONTENT OF NITROCELLULOSES PRODUCED BY THEM (SMALL AND HIGGINS[14])

Nitrogen, %	HNO_3, %	H_2SO_4, %	$HNOSO_4$, %	H_2O, %
10.52	22.30	51.97	5.25	20.48
10.74	22.08	52.50	5.10	20.32
10.86	21.60	53.13	4.80	20.47
10.96	22.13	51.99	5.60	20.28
11.05	23.86	51.24	5.17	19.73
11.10	22.74	52.04	5.57	19.65
11.14	24.81	53.60	1.37	20.22
11.19	23.80	50.40	6.55	19.25
11.91	20.18	55.93	6.00	17.89
11.92	20.15	55.80	6.20	17.85
11.96	20.30	56.13	5.80	17.77
11.98	19.98	55.95	6.25	17.82
12.06	20.50	55.45	6.40	17.65
12.75	19.54	60.92	4.57	14.97
13.00	20.00	59.64	5.30	14.16
13.30	24.37	59.54	4.86	11.23

and because many of the compositions exert a marked swelling or dissolving action on the fibers. In actual practice[14] (see Table 4) the different mixed acids used to produce the usual range of nitrocelluloses, with from about 10 to 13.5% N, do not vary very widely in composition from each other or from the H_2SO_4:HNO_3 ratio of 3 : 1 originally used by Schönbein nearly a century ago. The nature of the cellulosic material being nitrated also plays a part in determining the composition of mixed acid to be used. Thus, Schrimpff found that mixed acid must contain more nitric acid in order to nitrate wood pulp to the same extent as cotton.[9]

The rate of cellulose nitration increases with rise in temperature (see Table 5), but the drawback to much higher nitration temperatures than are normally employed is excessive degradation with resultant drop in vis-

cosity and yield.[14, 17] The commercial nitration of cellulose takes place much more rapidly than the other cellulose reactions which are practiced industrially; for most types, nitration is effected in about 30 minutes. The extreme rapidity of cellulose nitration,[22] particularly in the first few minutes, is shown well in Figure 4.

TABLE 5

EFFECT OF TEMPERATURE AND REACTION TIME ON THE NITRATION OF CELLULOSE (LUNGE AND COWORKERS[17])

Temp., °C.	Time, hr.	Nitrogen, %	Yield, %	Yield (calculated), %
0	0.5	10.71	152.3	153
0	7	13.19	173.3	174
10	7	13.37	175.8	176
15	7	13.38	175.6	176
19	0.5	12.72	166.1	170
19	7	13.39	175.6	176
40	0.5	13.07	172.3	173
40	7	13.06	169.6	173
60	0.5	13.08	169.2	173
60	4.5	13.07	162.1	173
80	0.25	13.07	161.2	173
80	0.5	13.12	125.2	173
80	3	13.12	81.5	173

NOTES: Nitration was effected with a 3:1 mixture of H_2SO_4:HNO_3.
Yields are based on the weight of cellulose employed; that is, the % yield is the weight of nitrocellulose obtained from 100 parts of cellulose.

The viscosity of nitrocellulose (that is, the viscosity of a solution of nitrocellulose at some standard concentration) is another important property, since it has a bearing on the use to which the nitrocellulose can be put and, also, on the mechanical properties of the substance in that use. Commercial nitrocelluloses are available in viscosities ranging from 15 to 377,000 centipoises (in 12.2% solution). The nitrocellulose viscosity may be influenced by a number of factors, including the viscosity of the original cellulose[2] and the nitration conditions. An increase in the H_2SO_4:HNO_3 ratio or a reduction in the ratio of mixed acid to cellulose (in the range from 80:1 to 30:1) will result in nitrocellulose of lower viscosity.[14] Viscosity will also be reduced by an increase in nitration time,[14, 23] nitra-

[22] E. B. Spalding, Hercules Powder Co., Parlin, N. J., private communication.
[23] K. Atsuki and M. Ishiwara, *Proc. Imp. Acad.* (*Tokyo*), **4**, 386 (1928).

tion temperature,[14, 24] or in the nitrosylsulfuric acid content of the mixed acid.[14]

For certain types of nitrocellulose the viscosity can be adequately regulated by controlling the various factors mentioned above. On the other

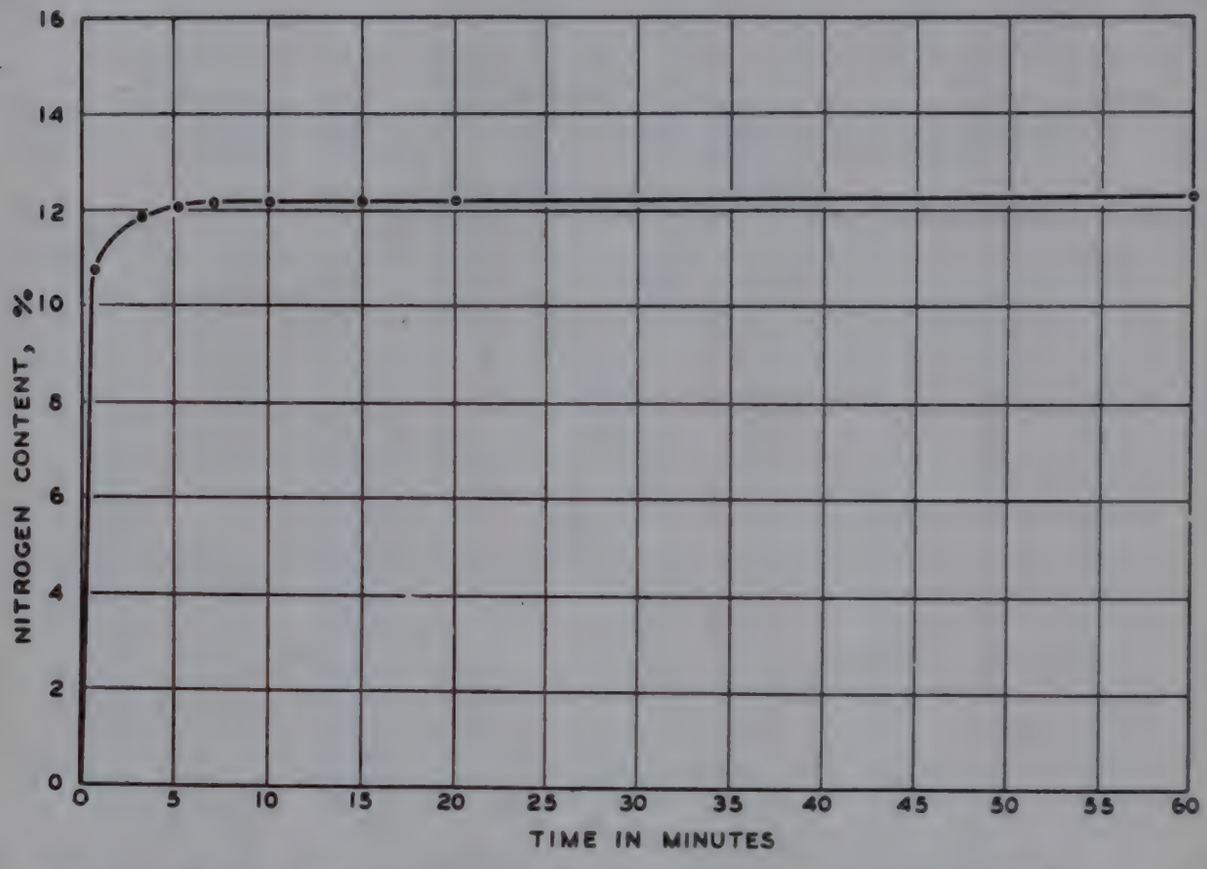

FIG. 4.—RATE OF NITRATION OF CELLULOSE IN A LABORATORY DIPPING POT WITH MIXED ACID CONTAINING 21.0% HNO_3, 61.5% H_2SO_4, AND 17.5% H_2O (SPALDING[22]).

hand, one of the major trends in nitrocellulose manufacture has been the production of increasingly lower-viscosity types to meet the demand of the lacquer industry for increase in the amount of nitrocellulose that can be dissolved in a lacquer without increasing the viscosity of the latter. This permits the deposition of a thicker coating in a single application and reduces the cost. The production of these low-viscosity types of nitrocellulose is usually carried out by a special treatment after nitration,[25, 26] although processes have been reported for reducing the viscosity of the cellu-

[24] K. Atsuki and M. Ishiwara, *J. Soc. Chem. Ind., Japan*, **31**, suppl. binding, 268 (1928).

[25] M. J. Callahan, *J. Soc. Chem. Ind.*, **47**, 232T (1928).

[26] R. Gabillion, *Rev. gén. mat. plastiques*, **7**, 259, 323 (1931); C. Stark, *Kunststoffe*, **21**, 151, 201 (1931); M. Pavlik, *Congr. chim. ind. Compt. rend. 17e Congr.*, Paris, Sept.-Oct. (1937), p. 1058.

lose before nitration.[11] The nitrocellulose may be treated with hot dilute solutions of acids or alkalies, or it may be digested in water under pressure. The rate of viscosity reduction on heating nitrocellulose under pressure in water at 132°C. is shown in Figure 5.[27]

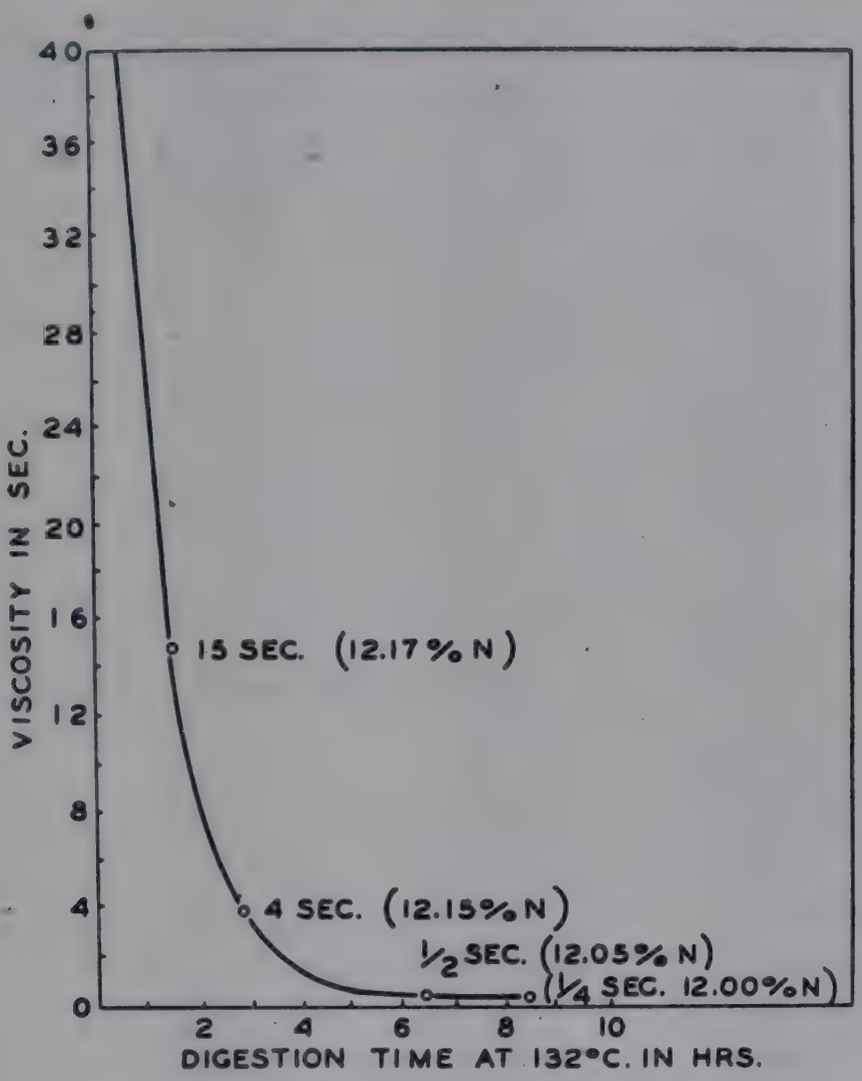

FIG. 5.—RATE OF VISCOSITY REDUCTION OF NITROCELLULOSE ON DIGESTION IN WATER AT 132°C. (MILLIKEN[27]).

The viscosities were determined in 12.2% solution by the Hercules method.[27a]

Nitration with Other Reagents. Considerable attention has been given to the use of nitration reagents other than HNO_3—H_2SO_4—H_2O, but none of them have attained industrial importance. The simplest of these reagents, of course, is aqueous nitric acid. The following data obtained by Vieille[28]

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[27] M. G. Milliken, *Ind. Eng. Chem.*, 22, 326 (1930).

[27a] *Nitrocellulose*. Hercules Powder Co., Wilmington, Del., 1939.

[28] P. Vieille, *Mém. poudres*, 2, 212 (1884–9).

indicate the extent of nitration that can be obtained with various concentrations of nitric acid:

% HNO_3	77.3	80.8	83.5	87.0	89.6	92.1	95.1
% N in nitrocellulose	6.85	8.07	8.78	10.33	11.53	12.23	12.68

Practically no nitration occurred with 75% nitric acid. In the approximate range of 80 to 85% nitric acid, the fibers dissolved completely and the nitrocellulose could be precipitated by adding water; other concentrations of HNO_3 swelled and gelatinized the fibers. Bouchonnet and coworkers[29] nitrated cellulose with pure HNO_3 and reported that the acid in the interior of the fibers is diluted by water formed in the reaction, which, together with the heat liberated, causes gelatinization or solution of some of the nitrocellulose. This partial or complete destruction of the fibers is a major drawback to the use of nitric acid as the sole reagent in the industrial nitration of cellulose. The addition of dehydrating salts to pure nitric acid prevents the hardening and contraction of fibers which occurs when HNO_3 is used alone. A maximum N content of 13.87% was obtained when 15 to 20% of NH_4NO_3 or 30% of KNO_3 was added to pure nitric acid as compared with 13.3% when HNO_3 was used alone. K_2SO_4, KH_2PO_4, and $NH_4H_2PO_4$ showed a similar action. The use of 97% HNO_3 was less satisfactory than pure HNO_3.

Attempts have been made to simplify the nitration of cellulose and to overcome the disadvantages in the use of nitric acid solutions by treating cellulose with HNO_3 vapor. Homogeneous nitrocelluloses with high stability were obtained by passing HNO_3 vapors through cellulose at reduced pressure while taking care to avoid condensation of HNO_3 and water vapors. Indications were obtained that the heat of reaction could be readily dissipated even in large-scale operations.[30] X-ray examination of nitrocelluloses prepared by this method showed that the reaction proceeds from the outside of the fiber to the inside. X-ray diagrams of products with 7.6 to 12.2% N had the appearance of mixtures of unreacted cellulose and cellulose trinitrate. The higher-substituted products (13% N and higher) appeared to be uniform.[31]

Nitrogen oxides have been used experimentally to nitrate cellulose. Pinck[32] found that nitrocellulose of any desired nitrogen content could be

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[29] A. Bouchonnet, F. Trombe, and G. Petitpas, *Compt. rend.*, **197**, 332 (1933); *Mém. poudres*, **28**, 277 (1938); *Bull. soc. chim.*, [5], **4**, 894 (1937).

[30] A. Bouchonnet, F. Trombe, and G. Petitpas, *Mém. poudres*, **28**, 308 (1938).

[31] G. Champetier and M. Foëx, *Compt. rend.*, **211**, 468 (1940).

[32] L. A. Pinck, *Ind. Eng. Chem.*, **22**, 1241 (1930).

prepared with a nitrating bath in which HNO_3 had been replaced by N_2O_4. An increase in the amount of N_2O_4 in the usual nitration mixture (HNO_3—H_2SO_4—H_2O) decreases the yield and nitrogen content of the nitrocellulose.[33] Treatment of cellulose directly with N_2O_4[34] or with N_2O_4 in the presence of H_3PO_4, $HClO_4$, HCl, and HCOOH results in oxidation without nitration.[35] The degree of nitration with N_2O_4—HNO_3 mixtures reaches a maximum at 30% N_2O_4.[35] Addition of nitrogen oxides to nitric acid (in absence of sulfuric acid) causes a higher degree of nitration (a maximum with N_2O_5); N_2O_3 and N_2O_4 cause greater depolymerization of cellulose than N_2O_5. Addition of 5% N_2O_5 to 95% HNO_3 yields nitrocellulose with 13.7% N compared to 13.0% N with 96% HNO_3 alone. The more vigorous action of N_2O_5 in comparison with P_2O_5 can be explained by the more rapid diffusion into the interior of the fiber and greater esterification in the interior by the HNO_3 resulting from the combination of N_2O_5 with water.[36] Dalmon and coworkers[37] treated cellulose with N_2O_5 dissolved in carbon tetrachloride at 130°C. for six hours in the dark and obtained a high yield of nitrocellulose with about 14% N. Treatment of dry cotton with pure N_2O_5 in a current of dry air or oxygen yielded pure cellulose trinitrate with 14.12% N.[38]

The replacement of sulfuric acid by phosphoric acid in nitrating acid has been studied because products of high stability are obtained. The nitrogen content of the nitrocellulose produced falls very rapidly as the water content of the HNO_3—H_3PO_4—H_2O mixture is increased.[39] In nitration with HNO_3—P_2O_5 mixtures the maximum nitrogen content of 14% was obtained in one hour; the optimum proportion of P_2O_5 seemed to be 25%.[40] Experiments to obtain nitrocellulose completely soluble in ether-alcohol showed that solubility is dependent on the extent of viscosity decrease. Berl and Rueff[41] nitrated cellulose with H_3PO_4—HNO_3 mixtures (anhydrous or containing a little P_2O_5) and obtained products of much higher viscosity and with greater nitrogen content than by nitration with

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[33] S. S. Mindlin and L. I. Kiez'mina, *J. Applied Chem.* (*U.S.S.R.*), **8**, 1415 (1935).

[34] E. C. Yackel and W. O. Kenyon, *J. Am. Chem. Soc.*, **64**, 121 (1942).

[35] P. P. Shorygin and E. V. Khait, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 188 (1937).

[36] Z. A. Rogovin and K. Tikhonov, *Cellulosechem.*, **16**, 11 (1935).

[37] R. Dalmon, J. Chéclin, and L. Brissaud, *Compt. rend.*, **201**, 664 (1935).

[38] R. Dalmon, *Compt. rend.*, **201**, 1123 (1935).

[39] C. K. Krauz and F. J. Blechta, *Chem. News*, **134**, 1, 17 (1927).

[40] F. Lenze and E. Rubens, *Z. ges. Schiess- u. Sprengstoffw.*, **26**, 4 (1931); **27**, 114, 154 (1932).

[41] E. Berl and G. Rueff, *Ber.*, **63B**, 3212 (1930); *Cellulosechem.*, **12**, 53 (1931); **14**, 115 (1933).

HNO_3—H_2SO_4 mixtures. Marked swelling facilitated the diffusion of the HNO_3, thus leading to uniform nitration; the products had high stability. The disadvantages of this process include the need for using anhydrous mixed acid and the high cost of phosphoric acid. Under certain conditions, nitration with HNO_3—H_3PO_4—P_2O_5 was very rapid and a very highly nitrated nitrocellulose (13.5% N) was obtained in 1.5 minutes.[42] Bouchonnet and coworkers[43] found that a mixture of nitric acid (92 parts) and HPO_3 (8 parts), or mixtures containing slightly more water, gave products of about 13.5% N, which, after stabilization by boiling with water, were satisfactory for guncotton. A comprehensive study of nitration with mixtures of phosphoric and nitric acids was carried out at Poudrerie Nationale d'Angoulême in France.[44] They concluded that this method is not suitable for the production of nitrocellulose with about 12% N (CP_2 guncotton) because small divergences from the optimum nitrating composition have an adverse effect on the product. It can be used satisfactorily for preparing nitrocellulose with 13.7% N (CP_1 guncotton).

Nitration with mixed acids containing organic diluents has also been investigated. Nitration with a mixed acid emulsion containing carbon tetrachloride or pentane and stabilized with a few drops of naphthalenesulfonic acid, yielded products with about 11% N and fairly good solubility; the acid mixture contained much less HNO_3 and H_2SO_4 than usual.[45] To avoid the gelation of fibers which occurs on nitrating cellulose with concentrated HNO_3 alone, Trogus[46] used a mixture of HNO_3 and glacial acetic acid. To obtain nitrocelluloses with over 12.5% N, it was advantageous to have present a small amount of water-binding agent such as acetic anhydride or P_2O_5. Darzens[47] nitrated cellulose with a homogeneous mixture of HNO_3—$(CH_3CO)_2O$—$CHCl_3$ and obtained a product with 13.7% N. Further study of this process showed that nitration is effected very slowly and that the products are insoluble in ether-alcohol.[48] Cellulose trinitrate (14.14% N) was obtained by treating cotton linters with a mixture containing 50% HNO_3, 25% acetic acid, and 25% acetic anhydride for five hours at 15°C. and then extracting the product with boiling

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[42] E. Berl and G. Rueff, *Cellulosechem.*, **14**, 109 (1933).

[43] A. Bouchonnet, F. Trombe, and G. Petitpas, *Bull. soc. chim.*, [5], **4**, 560 (1937).

[44] Poudrerie Nationale d'Angoulême, *Mém. poudres*, **28**, 82 (1938).

[45] Z. A. Rogovin and P. Paradnya, *Cellulosechem.*, **15**, 32 (1934).

[46] C. Trogus, *Ber.*, **64B**, 405 (1931).

[47] G. Darzens, *Mém. poudres*, **25**, 437 (1932–3).

[48] L. Brissaud, *Mém. poudres*, **25**, 440 (1932–3).

alcohol in a Soxhlet extractor; stability was satisfactory.[49] It should be pointed out that the use of mixtures of HNO_3 and acetic anhydride can be very dangerous because of the formation of acetyl nitrate which explodes at elevated temperatures.

Mechanism of Cellulose Nitration. According to evidence presented by Berl and coworkers[50] and other investigators,[51, 52] cellulose nitration involves the usual principle of esterification; that is, when molecular quantities of an acid and an alcohol react, an ester is formed and water is split out. Since the reverse reaction also takes place at the same time, an equilibrium will be set up among acid, alcohol, water, and ester. The reaction is forced to completion by displacement of the equilibrium when an excess of one component (in this case, the acid) is used, and the water formed combines with the H_2SO_4. This equilibrium between the nitrocellulose and the nitrating medium has been found to occur over a wide range of substitution, the nitrogen content of the nitrocellulose being determined by the final composition of the nitrating bath rather than by the composition of the original mixed acid. The evidence of the existence of this equilibrium includes the observation that the equilibrium can also be approached from the other direction; that is, long contact of nitrocellulose with relatively dilute mixed acid causes partial denitration and production of a nitrocellulose with the same nitrogen content as would be obtained by direct action of this mixed acid on cellulose.

Various investigators have attempted to determine the properties of mixed acids which influence their nitrating capacity. Sapozhnikov[53] determined the nitric acid vapor pressure of various mixed acids and the nitrogen content of the nitrocelluloses produced by them. He made the striking observation that there is a close relation between these values and found that the highest nitrogen content was attained with the mixed acid having the highest HNO_3 vapor pressure. He also found that the nitric acid vapor pressure in the mixed acid rises to a maximum on the addition of sulfuric acid and that the latter combines with water until the nitric acid is present only as HNO_3. Further addition of sulfuric acid results in

[49] A. Bouchonnet, F. Trombe, and G. Petitpas, *Compt. rend.*, **197**, 63 (1933); *Mém. poudres*, **28**, 295 (1938).

[50] E. Berl and R. Klaye, *Z. ges. Schiess- u. Sprengstoffw.*, **2**, 403 (1907); E. Berl and E. Berkenfeld, *Z. angew. Chem.*, **41**, 130 (1928); E. Berl and O. Hefter, *Cellulosechem.*, **14**, 65 (1933).

[51] P. Demougin and Bonnet, *Mém. poudres*, **24**, 147 (1931).

[52] K. Fabel and H. Fritzsche, *Nitrocellulose*, **10**, 3, 24 (1939).

[53] A. Sapozhnikov, *Z. ges. Schiess- u. Sprengstoffw.*, **1**, 453 (1906); **4**, 441, 462 (1909); see also C. Kullgren, *Z. ges Schiess- u. Sprengstoffw.*, **3**, 146 (1908).

dehydration of HNO_3 whereby the latter is rendered inactive. Sapozhnikov obtained the highest degree of cellulose nitration with the maximum concentration of sulfuric and nitric acids which still permits the latter to exist as HNO_3. The lowest degree of nitration was obtained with a mixed acid which had the lowest HNO_3 vapor pressure and which, in Sapozhnikov's opinion, contained the nitric acid as the hydrate $HNO_3 \cdot H_2O$.

Berl and coworkers[18] confirmed and extended the work of Sapozhnikov. They pointed out that, according to their triangular diagram (Fig. 2) in which the points corresponding to HNO_3 vapor pressure maxima are joined by the broken line, there is an increase in nitrogen content with decrease in water content on approaching the broken line and that the maximum nitration is attained with a spent acid whose composition lies on this line. This composition corresponds to:

66.0% H_2SO_4 (40 mole %)
21.8% HNO_3 (20 mole %)
12.2% H_2O (40 mole %)

This is exactly equivalent to a ratio of $1HNO_3 : 2(H_2SO_4 \cdot H_2O)$.

While various explanations have been offered of the role of sulfuric acid in the nitration reaction, there is no reason to believe that it performs any other useful function than that of dehydration. This view is supported by the knowledge that cellulose can be nitrated equally well by nitric acid containing other dehydrating agents such as nitric anhydride, phosphoric anhydride, or acetic anhydride. In fact, cellulose can be nitrated to some extent by nitric acid alone (as was shown above), and, if steps are taken to remove the water formed in the reaction, as is the case when cellulose is treated with HNO_3 vapors under reduced pressure, products with 13.6% N can be readily obtained.[30]

The failure to attain in practice the theoretical N content of 14.14% with HNO_3—H_2SO_4—H_2O mixtures can be best explained by the ability of the H_2SO_4 to enter into the esterification reaction in competition with the nitric acid and the resultant formation of sulfuric-nitric mixed esters.[54] The formation of such mixed esters has been observed by many investigators.[55, 56, 57] Farmer[58] has attempted to explain the failure to attain complete nitration, and other nitration phenomena, on the basis that esterifica-

[54] K. A. Hofmann, *Sitzber. preuss. Akad. Wiss. Physik.-math. Klasse*, **1933**, 800.
[55] C. F. Cross, E. J. Bevan, and R. L. Jenks, *Ber.*, **34**, 2496 (1901).
[56] C. N. Hake and M. Bell, *J. Soc. Chem. Ind.*, **28**, 457 (1909).
[57] A. Hervé, *Le Moniteur Scientifique Quesneville*, [5], **8**, 193 (1918).
[58] R. C. Farmer, *J. Soc. Chem. Ind.*, **50**, 75T (1931).

tion with nitric acid proceeds most readily through its "pseudo" form ($O_2N \cdot OH$). He suggested that in the concentrated mixed acids needed for maximum nitration of cellulose, the nitrating action is suppressed by the formation of nitronium sulfate, $(HO)_3N(SO_4H)_2$, and that the resulting removal of part of the pseudonitric acid prevents the formation of cellulose trinitrate.

The formation of intermediate compounds during the nitration of cellulose has been studied by various investigators. Katz, Hess, and Trogus[59, 60, 61] found that the $[C_6H_{10}O_5 \cdot HNO_3]_x$ addition compound reported by Knecht[62] has a constant composition (as indicated by the formula) and a characteristic x-ray diagram; on washing with water, this addition compound yields a regenerated cellulose with the x-ray diagram of mercerized cellulose. Miles[63] found that the x-ray diagram of fibers obtained by denitrating nitrocelluloses of Classes I and II (see Miles and Craik[64]) shows them to consist almost entirelv of mercerized cellulose. It is therefore probable that some constituent of the nitrating mixture must have penetrated the whole structure. The results of Katz and Hess[59] suggest that it is the HNO_3 that must penetrate the micelle. Carrière[65] found a higher HNO_3:H_2SO_4 ratio in the water in which nitrocellulose is drowned after nitration than in the wringer acid and suggested that a "pernitrocellulose," having more than the theoretical nitrogen content for cellulose trinitrate, is formed during nitration and decomposed on contact with water. Demougin and Bonnet[66] studied this phenomenon and obtained results which indicate that an adsorption product is obtained but not a chemical compound. Berl and Rueff[67] treated nitrocellulose with pure HNO_3 or mixed acids and obtained an adsorption product (14.8% N) similar to that of Knecht[62]; water decomposed it to nitrocellulose and HNO_3. X-ray diagrams, after treatment of cellulose with dry HNO_3, showed spots due to cellulose, nitrocellulose, and Knecht's compound.

Two general concepts have been advanced to explain the manner in which the nitration reaction takes place in cellulose fibers.[68] According

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[59] J. R. Katz and K. Hess, *Z. physik. Chem.*, **122**, 126 (1926).
[60] C. Trogus, *Cellulosechem.*, **15**, 104 (1934).
[61] C. Trogus and K. Hess, *Z. Elektrochem.*, **40**, 193 (1934).
[62] E. Knecht, *Ber.*, **37**, 549 (1904).
[63] F. D. Miles, *Trans. Faraday Soc.*, **29**, 110 (1933).
[64] F. D. Miles and J. Craik, *Nature*, **123**, 82 (1929); *J. Phys. Chem.*, **34**, 2607 (1930).
[65] E. Carrière, *Bull. soc. chim.*, [4], **39**, 438 (1926).
[66] P. Demougin and Bonnet, *Mém. poudres*, **24**, 157 (1931).
[67] E. Berl and G. Rueff, *Cellulosechem.*, **14**, 97 (1933).
[68] K. Fabel, *Nitrocellulose*, **11**, 223 (1940); **12**, 3 (1941).

to the first of these concepts, the nitration reagent penetrates between the cellulose micelles and nitration proceeds progressively from the outside to the interior of the micelle (micellar heterogeneous reaction). The second concept, which has received widest acceptance, suggests that the nitration reagent penetrates uniformly into all parts of the cellulose fiber and all the molecules are nitrated at approximately the same time (homogeneous or permutoid reaction).

On the basis of x-ray examination of the structure of different specimens of nitrocellulose, Herzog and von Náray-Szabó,[69] and von Susich[70] claimed that all nitrocelluloses (below the trinitrate) are made up of mixtures of cellulose trinitrate and unchanged cellulose, and they suggested that the nitration of cellulose is a heterogeneous reaction. Hess and Trogus,[61, 71] who have been the chief supporters of this theory, expressed the further belief that all esterification reactions of cellulose, including nitration, are micellar heterogeneous and are not of the homogeneous type. Sakurada and coworkers[72, 73] proposed the following equation to cover all micellar heterogeneous reactions including cellulose nitration:

$$x = kz^m \qquad (1)$$

in which x = amount of cellulose reacted, z = reaction time, and k and m = constants (see Section A of this chapter). Chemical and x-ray analyses confirm, in their opinion, the view that the kinetics of cellulose nitration are determined by the velocity of diffusion rather than by the velocity of nitration. Tomonari[74] has claimed that the mechanism of the reaction is dependent on the composition of the mixed acid. With mixed acid very low in water content, the reaction is micellar heterogeneous because the rate of nitration is greater than the rate of diffusion; with acid mixes of high water content, the reaction approaches the permutoid type because of the greater speed of diffusion.

The overwhelming mass of evidence on this subject favors the permutoid theory of cellulose nitration. This evidence includes the conclusion, based on the work of Berl and coworkers[50] and others,[51, 52] that an equilibrium

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[69] R. O. Herzog and S. von Náray-Szabó, *Z. physik. Chem.*, **130**, 616 (1927).

[70] S. von Náray-Szabó and G. von Susich, *Z. physik. Chem.*, **134**, 264 (1928).

[71] K. Hess and C. Trogus, *Z. physik. Chem.*, **B15**, 157 (1931).

[72] I. Sakurada and M. Shojino, *J. Soc. Chem. Ind., Japan*, **35**, suppl. binding, 287 (1932); **36**, suppl. binding, 306 (1933).

[73] T. Nakashima, H. Nakahara, and I. Sakurada, *J. Soc. Chem. Ind., Japan*, **39**, suppl. binding, 51 (1936).

[74] T. Tomonari, *J. Soc. Chem. Ind., Japan*, **37**, suppl. binding, 478, 654, 772, 775 (1934); **38**, suppl. binding, 58, 62 (1935).

exists between the nitrating medium and the nitrocellulose over a large range of composition. Despite the fact that equilibrium may be reached slowly when proceeding from a higher to a lower nitrogen content, the final nitrogen content is independent of time and can be changed to a higher or lower constant value by immersion in another mixed acid. The existence of this equilibrium is in harmony with the permutoid theory of nitration only.

Opposition to the micellar heterogeneous theory of cellulose nitration has also resulted from the failure to find any appreciable amount of unchanged cellulose in the examination of hundreds of nitrocellulose samples.[75] In other fractionation experiments with numerous nitrocellulose specimens, none of the fractions varied more than 0.3% in nitrogen content from the starting material; also no evidence was obtained of the presence of cellulose trinitrate in any of the samples.[63] N. K. Adam[76] has shown that nitrocellulose solutions spread to form monomolecular films of nitrocellulose on 2 *N* NaOH solution. In discussing these results, Miles[63] has pointed out that, if nitrocelluloses are constituted as claimed by Hess and Trogus,[71] either the micelle must solvate or disperse as such, in which case it seems impossible to account for the spreading to the thickness of one molecule; or, the cellulose trinitrate must separate from the cellulose core since there is no reason for believing that the cellulose would disperse. If the latter case were true, only the cellulose trinitrate would spread and the measured film area for nitrocellulose of 10.4% N would be 35% less than was actually found, an error which could hardly be undetected.

Miles and Craik[63, 64] examined by x-ray diffraction methods a series of nitrocelluloses, prepared with various HNO_3—H_2SO_4—H_2O mixtures, and the corresponding denitrated products. They divided the products into three classes depending on the position on the diagram (Fig. 3) of the mixed acid from which they were prepared: (1) N content less than 7.5%, fiber structure unimpaired, insoluble in all organic solvents; (2) N content 7.5–10.5%, fiber structure more or less impaired, swell or dissolve in acetone; (3) N content over 10.5%, fibrous, dissolve completely in acetone, comprise all technical nitrocelluloses. Miles and Craik were unable to confirm the conclusion of Herzog and coworkers that nitrocelluloses are to be regarded as mixtures of cellulose trinitrate and unchanged cellulose. To account for their results, Miles and Craik presented the following picture of cellulose nitration. In the first stage of nitration, only the diffractions of almost completely mercerized cellulose were observed, and they therefore suggested

[75] H. Brunswig, *Z. ges. Schiess- u. Sprengstoffw.*, **23**, 337, 384 (1928).

[76] N. K. Adam, *Trans. Faraday Soc.*, **29**, 95 (1933).

that the OH groups in the "inner surface" of the fiber were nitrated while those in the interior of the micelles were not nitrated; that is, the reaction is heterogeneous. With a more concentrated nitration mixture, a greater area of the surface is affected so that in nitrations of Class 2 the number of unchanged cellulose chains is too small for definite diffraction and the micellar arrangement is almost entirely broken down. In Class 3, the swelling and micellar disarrangement decreases as the concentration of the acid increases. With increase in concentration of the acid, the number of nitrate groups introduced increases, but with only approximate regularity, so that definite crystallization is difficult at first but becomes less so with increasing substitution, until at about 12.8% N the cellulose trinitrate diagram appears. The essential feature of this picture is that in nitrations of Classes 2 and 3 the nitrate groups are so distributed among the chain molecules that there is little likelihood of any one molecule being completely nitrated to the trinitrate before the rest; that is, the reaction is permutoid.

Miles[63] also pointed out that Hess and Trogus[71] based their belief that cellulose nitration is a micellar heterogeneous reaction on the examination of nitrocelluloses (7 to 13% N) prepared by the somewhat unusual procedure of nitrating ramie for various periods (1 to 480 minutes) with a single anhydrous nitrating mixture containing 29.7% HNO_3 and 70.3% H_2SO_4. It seems doubtful that the examination of these nitrocelluloses would give information of much value about the nature of the reaction which takes place in commercial nitration, because in the latter case the reaction is carried out practically to completion and the nitrogen content is controlled primarily by the mixed acid composition and not by the reaction time.

Stability and Stabilization. A point of major importance in the chemistry of nitrocellulose is the fact that its usefulness in explosives or in ordinary articles of commerce depends a great deal upon its stability, that is, upon its ability to resist decomposition after long periods of time under various conditions. Thus, in guncotton, the decomposition of unstable nitrocellulose during storage can accelerate to the point at which the nitrocellulose will explode with great violence. The use of unstable nitrocellulose will result in gradual embrittlement and disintegration of films; in coated cloth (artificial leather) the coatings will embrittle, then crack and peel off; while in lacquers the instability will cause corrosion of the metal on which the lacquer has been applied.[14, 77]

In the first years of the development of the manufacture of nitrocellulose,

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[77] J. B. Wiesel. *Paint, Oil Chem. Rev.*, **80**, No. 10, 8 (1925).

which were devoted almost exclusively to the production of guncotton, a number of disastrous explosions occurred which were caused by the instability of the product. The search for the causes of this instability resulted in the discovery by Abel,[78] about eighty years ago, that retention of traces of the nitrating acid by the nitrocellulose can cause instability. Wiggam[79] has more recently shown that the stability of nitrocellulose is lowered to an extent dependent upon the amount of acid remaining absorbed. As was pointed out before, the formation of sulfuric acid esters of nitrocellulose during nitration was recognized early in this century.[55, 56] Hake and Lewis[80] were among the first to suggest that the instability of nitrocellulose is due to the gradual splitting off of the unstable sulfate groups. The formation of these sulfuric acid esters, and hence the stability, was found to vary with the composition of the nitrating acid mixture. The combined sulfate content was found to increase with increase in (a) nitration time,[56] (b) H_2SO_4:HNO_3 ratio in the mixed acid,[56, 57] and (c) nitrosylsulfuric acid content of the mixed acid.[81] An increase in the water content of the mixed acid increased the stability of the nitrocellulose produced.[81, 82] It is interesting to note that when the formation of sulfuric acid esters of cellulose is avoided, as in nitration with HNO_3 vapors, nitrocelluloses of high stability are obtained by merely washing the products with cold water.[30]

In addition to combined sulfate groups, instability in nitrocellulose may be caused by the decomposition of cellulose esters of nitrous acid or of nitrated degradation products of cellulose.[83] The presence of impurities (which could be extracted with methanol) in a lot of commercial linters was also found to decrease the stability of the nitrocellulose made from those linters.[81]

Various methods have been developed to improve the stability of nitrocellulose. Abel undertook the study and manufacture of guncotton for the British Government in 1863. Following his discovery of the effect of retained acid on stability, he found that pulping of guncotton in a paper beater considerably reduced the fiber length of the nitrated cotton and thus permitted ready removal of the retained acid by washing.[78] In the Abel

[78] F. Abel, Brit. Patent 1102 (1865); see also E. C. Worden, *Technology of Cellulose Esters*, Vol. I, Part 3, p. 1604 *et seq.* (ref. 1, p. 622).

[79] D. R. Wiggam, *J. Phys. Chem.*, **35**, 536 (1931).

[80] C. N. Hake and R. J. Lewis, *J. Soc. Chem. Ind.*, **24**, 374, 914 (1905).

[81] E. Berl and G. Rueff, *Cellulosechem.*, **14**, 109 (1933).

[82] T. Tomonari, *J. Soc. Chem. Ind., Japan*, **37**, suppl. binding, 511 (1934); **38**, suppl. binding, 326 (1935).

[83] E. Berl and M. Delpy, *Z. ges. Schiess- u. Sprengstoffw.*, **8**, 129 (1913).

process, the washing was carried out with alkaline water in order to bring the nitrocellulose to neutrality as rapidly as possible. A further advance in stabilization was achieved with the discovery by Robertson[84] in 1905 that the unstable sulfuric acid esters of nitrocellulose are more readily decomposed by steeping the nitrocellulose in boiling water, while it still retains a small amount of mixed acid, than by Abel's treatment with boiling alkaline water. It is probable that the acid treatment also causes decomposition of other unstable ester groups. At equal concentrations, the stabilizing action of the following acids in the wash water decreases in this order: HNO_3, HCl, and H_2SO_4.[85]

As has been indicated, nitrocellulose cannot be satisfactorily stabilized by washing with alkaline water directly after nitration. However, if nitrocellulose which has been stabilized by an acid boil is then treated with water containing $CaCO_3$ (for example, hard water), a further improvement in stability results.[86, 87, 88] This behavior is explained by the fact that the residual combined sulfuric acid in cellulose esters exists in the form $RO \cdot SO_2OH$ which is readily hydrolyzed by water or acids but which becomes $RO \cdot SO_2OM$ in presence of inorganic bases, toward which it is very stable.[89] This salt is stable even to dilute acids, since it is possible to remove any excess carbonate by treating the nitrocellulose with 0.1 *N* HCl at moderate temperature without destroying the salt.[87]

Improvement in the stability of nitrocellulose, apparently by removal of unstable impurities and degradation products,[83] has been effected by extraction with alcohols under various conditions,[81, 90, 91] including the commercial dehydration of nitrocellulose with ethyl alcohol.[14]

The development of materials (stabilizers) to be added to nitrocellulose to combine with the acidic products of decomposition and so prolong its life has proceeded parallel with the development of stabilization and purification treatments.[92] To be satisfactory, the stabilizer should absorb the products of nitrocellulose decomposition, be completely compatible with the nitrocellulose, and at the same time be so inert as not to react with it.

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[84] R. Robertson, *J. Soc. Chem. Ind.*, **25**, 624 (1906).

[85] P. Demougin and M. Landon, *Mém. poudres*, **27**, 182 (1937).

[86] J. Goujon, *Mém. artillerie française*, **8**, 837 (1929).

[87] M. Landon, *Mém. poudres*, **27**, 190 (1937).

[88] A. Breguet and A. Caille, *Bull. soc. chim.*, [4], **35**, 680 (1924).

[89] J. F. Briggs, *J. Soc. Chem. Ind.*, **25**, 626 (1906).

[90] H. Muraour, *Bull. soc. chim.*, [4], **51**, 1089 (1932).

[91] F. Langenscheidt, *Z. ges. Schiess- u. Sprengstoffw.*, **9**, 54 (1914).

[92] A. Marshall, *Explosives*. P. Blakiston's Son & Co., Philadelphia; Vol. II (1917), p. 640; Vol. III (1932), p. 210.

Basic inorganic compounds, such as $CaCO_3$, were among the first materials used as stabilizers. It should be noted that $CaCO_3$ will react with nitrocellulose under certain conditions and actually reduce its stability.[93, 94] Solvents such as amyl alcohol were used in France for some time as stabilizers but were superseded by less volatile compounds. Mineral jelly was found to have a strong stabilizing action which is apparently due to the ability of unsaturated compounds contained in the jelly to react with nitrogen oxides.

The best stabilizers are weak organic bases, such as amines and urea derivatives. Diphenylamine ranks very high as a stabilizer even though it is not a solvent for nitrocellulose; it has been in wide use for many years. However, evidence has been obtained showing that diphenylamine attacks nitrocellulose[95] and that this reaction is catalyzed by copper salts such as are frequently found in nitrocellulose[96]; *p*-nitrodiphenylamine behaves in the same way.[96] When diphenylamine reacts with nitrocellulose, nitrosodiphenylamine and some strongly colored secondary products are formed Nitrosodiphenylamine was found to be a better stabilizer than diphenylamine; in further contrast to the latter, it can gelatinize nitrocellulose and therefore remains intimately mixed with it.[97] Urea has been used for some time as a stabilizer in celluloid, but it also reacts with nitrocellulose, and its use in smokeless powder was therefore discontinued. Derivatives of urea have been tested as stabilizers, and Marshall[98] expressed the belief in 1932 that *sym*-diethyldiphenylurea (Centralite I), which is also an efficient gelatinizing agent for nitrocellulose, is the best stabilizer known. Unlike diphenylamine, Centralite I has no active H atoms and it therefore does not react with nitrocellulose.[96]

It is apparent, from the results of many investigations on the mechanism of decomposition of nitrocellulose, that this decomposition takes place in two stages. In the first stage, the reaction is relatively slow; in the second stage, the initial decomposition products react with the nitrocellulose, and the reaction becomes autocatalytic and therefore accelerates rapidly. If the products of decomposition in the first stage are removed as rapidly as formed (for example, by a stabilizer), the reactions of the second stage are

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[93] A. Koehler and M. Marqueyrol, *Mém. poudres*, **23**, 11 (1928).

[94] P. Demougin, *Mém. poudres*, **26**, 119 (1934–5).

[95] T. L. Davis and A. A. Ashdown, *Ind. Eng. Chem.*, **17**, 674 (1925).

[96] H. Muraour, *Bull. soc. chim.*, [5], **3**, 2240 (1936).

[97] M. Marqueyrol, *Mém. poudres*, **23**, 158 (1928).

[98] A. Marshall, *Explosives*, Vol. III, p. 210; see ref. 92, p. 642.

prevented, and the decomposition is held down to a relatively slow rate.[97, 99]

Since nitrocellulose decomposes rather slowly at room temperature, a wide variety of stability tests have been devised in which the nitrocellulose is heated to accelerate decomposition and so to give an advance indication of the stability behavior of a particular lot of nitrocellulose on storage.[100] Wide differences in the bases of these tests have led to differences in the interpretation of stability behavior. Another fact of importance in considering the results of heat stability tests is that they do not merely accelerate a phenomenon which occurs at room temperature and therefore do not give an exact picture of the changes which occur in nitrocellulose on aging at room temperature.[101]

In the decomposition of nitrocellulose at room temperature, hydrolysis is caused by traces of acid which have not been completely washed out or which result from the decomposition of unstable ester groups. The hydrolysis results in scission of the cellulose chain and the splitting off of nitrate groups. If the nitrogen oxide decomposition products are removed as rapidly as formed (for example, by a stabilizer) and thereby are prevented from reacting with the nitrocellulose the decomposition proceeds rather slowly and not with the increasing velocity that otherwise results.[101]

At elevated temperatures, another reaction takes place in the decomposition of nitrocellulose; this is the internal combustion of some of the glucose anhydride groups with resultant scission of the cellulose chain. If the nitrogen oxides are not removed, they form with the water present a solution of nitric and nitrous acids which form the medium for the following secondary reactions: (a) oxidation of glucose units, (b) hydrolysis of nitrate groups, and (c) hydrolytic scission of the cellulose chain.[102, 103]

Moisture content plays an important part in the decomposition of nitrocellulose by hydrolysis. According to Muraour,[104] water exerts no action

[99] G. de Bruin, *Études Sur La Décomposition Spontanée De La Poudre Sans Fumée, II.* Communiqué de la Soc. Anon. Fabriques Néerlandaises D'Explosifs, No. 2, Amsterdam, May, 1924.

[100] For a review of stability tests, see A. Marshall, *Explosives*, Vol. II, p. 644 and Vol. III, p. 213; see ref. 92, p. 642.

[101] H. Muraour, *Chimie & industrie*, **20,** 610 (1928); *Bull. soc. chim.*, [4], **47,** 1259 (1930).

[102] J. Desmaroux, *Compt. rend.*, **194,** 1649 (1932); **196,** 1394 (1933).

[103] J. Desmaroux, R. Vandoni, L. Brissaud, and T. Petitpas, *Mém. poudres*, **29,** 134 (1939).

[104] H. Muraour, *Bull. soc. chim.*, [4], **49,** 276 (1931); **51,** 1094 (1932); see also G. de Bruin and P. F. M. de Pauw, *Études Sur La Décomposition Spontanée De La Poudre Sans Fumée, IV.* Communiqué de la Soc. Anon. Fabriques Néerlandaises D'Explosifs, No. 4, Amsterdam, Oct., 1925.

at 15 to 20°C. on suitably prepared nitrocellulose even after 20 to 30 years. At 50 to 75°C. in a humid atmosphere, the deterioration of nitrocellulose is rapid; the initial hydrolysis of the ester causes formation of dilute nitric acid which by further hydrolysis causes rapid decomposition of nitrocellulose. The action of HNO_3 on nitrocellulose is strongly dependent on its concentration. A decrease in the moisture content (but not to complete dryness) of smokeless powder containing even a trace of free acid may cause an increase in the rate of decomposition. A large amount of water dilutes the HNO_3 and thereby retards or completely stops the decomposition. A minimum concentration of HNO_3 is necessary to produce hydrolysis.

(*b*) *Commercial Manufacture of Nitrocellulose*[105, 106, 107]

In the direct dipping process, which was used in the early days of nitrocellulose manufacture, the cotton was dipped in the mixed acid and, after nitration was complete, it was transferred by hand to a centrifuge where the spent acid was removed. In a later development, nitration was carried out directly in a centrifuge which was rotated slowly to cause circulation of the acid; when nitration was complete, the centrifuge was rotated more rapidly and the spent acid was removed. The nitrocellulose was then transferred with aluminum forks to washing tubs.[108]

The Thomson displacement process attained large-scale operation in England, where it was developed for the manufacture of guncotton. In this process, pans with perforated false bottoms are filled with mixed acid; then cotton is added and covered with a perforated plate so that the cotton is completely submerged. At the end of nitration, the spent acid is drained off slowly and is displaced at the same time with water. The advantages claimed for this process include: (a) low power consumption, (b) no moving parts, hence low investment in equipment, (c) low maintenance cost, and (d) practically complete recovery of all acid.[108]

The most widely used process, in recent years, is the so-called mechanical dipper process,[109, 110, 111] which was developed by the du Pont Company.

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[105] R. Escales, *Die Schiessbaumwolle.* Veit & Comp., Leipzig, 1905.

[106] C. Stark, *Die Collodiumwolle.* M. Krayn, Berlin, 1931.

[107] G. Bonwitt, *Das Celluloid und seine Ersatzstoffe.* Union Deutsche Verlagsges., Berlin, 1933.

[108] F. L. Nathan, *J. Soc. Chem. Ind.*, **28**, 177 (1909).

[109] J. R. du Pont, *Chem. & Met. Eng.*, **26**, 11 (1922).

[110] A. B. Nixon, *Hercules Mixer*, **8**, 55 (1926).

[111] E. P. Partridge, *Ind. Eng. Chem.*, **21**, 1044 (1929).

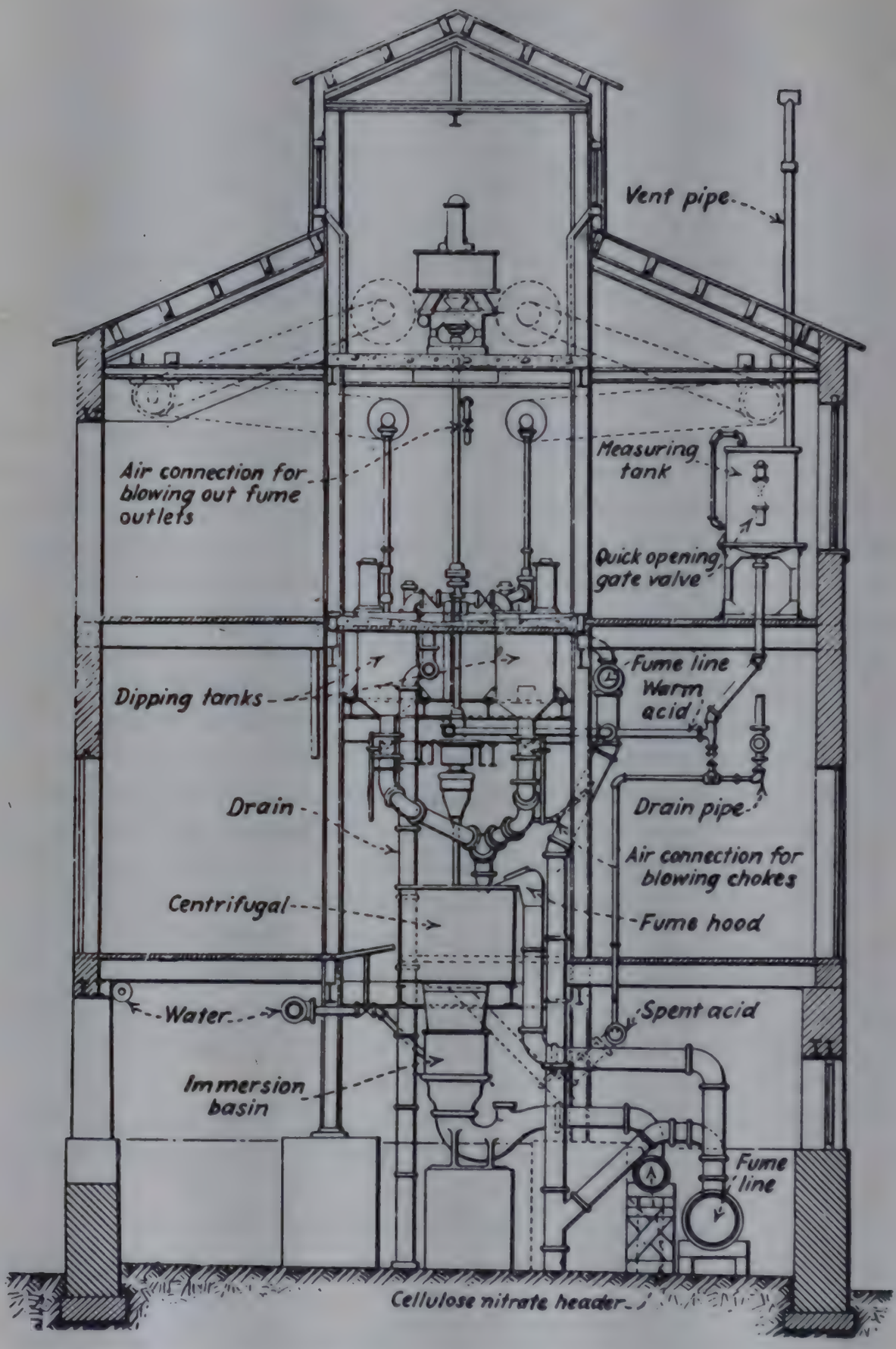

FIG. 6.—NITRATING BUILDING AND EQUIPMENT FOR THE MECHANICAL DIPPER PROCESS OF NITRATION (DU PONT[109]).

A sketch of the nitration building and equipment is shown in Figure 6. The dippers consist of cylindrical tanks made of an acid-resistant steel alloy and fitted with two stirrers. A pipe of large diameter, closed by a valve, leads from the bottom of the dipper to a centrifuge on the floor below. Four dippers and one centrifuge form a unit in this process. The cellulose to be nitrated, in suitable physical form, is dried to a moisture content of less than 1%. The drying operation is important because excessive moisture in the cellulose results in: (a) lower degree of nitration than planned due to dilution of the mixed acid, (b) poor solubility because of irregular nitration, and (c) temperature rise on dipping which causes disintegration of fibers and loss in yield.[14, 109] The dried cellulose is delivered in weighed lots of about 30 pounds to the mechanical dippers. About 1600 pounds of mixed acid of selected composition is charged at a definite temperature into the dipper from a measuring tank, and the cellulose is then added. The latter is quickly wetted and submerged as a result of the mechanical agitation. After about 30 minutes of nitration, the bottom valve is opened and the mixture of spent acid and nitrocellulose is discharged directly into the centrifuge, where most of the spent acid is removed in about five minutes. In general, about one pound of acid is retained by each pound of nitrocellulose in the centrifuge. The nitrocellulose is discharged through an opening in the bottom of the centrifuge into a volume of water which thoroughly drowns the nitrocellulose and is large enough to prevent any appreciable rise in temperature. The nitrocellulose is then floated through a flume line to the purification area. The spent acid leaving the centrifuge is accumulated and brought back to proper strength for re-use in nitration by the addition of strong nitric and sulfuric acids. This process yields a very uniform product because of the agitation during nitration and requires a minimum amount of manual labor. According to Stettbacher,[112] most of the large manufacturers of nitrocellulose in Europe have converted their plants from the centrifuge process to the mechanical dipper process.

Purification and stabilization of the nitrocellulose is carried out in large wooden tubs lined with chrome-steel sheet and fitted with agitators. These tubs, which can hold as much as 12,000 pounds of nitrocellulose, are also equipped with a perforated false bottom under which steam lines are uniformly distributed. After the nitrocellulose has been washed to a predetermined acidity, the tubs are filled with water which is heated to boiling by admitting live steam. This stabilization treatment may consist of one continuous boil or it may consist of a series of short boils with frequent

[112] A. Stettbacher, *Die Schiess- und Sprengstoffe*. 2nd ed., J. A. Barth, Leipzig, 1933, p. 134.

changes of water. Depending on the type of nitrocellulose being manufactured, boiling and agitation are continued for 10 to 60 hours. For some types, the nitrocellulose is also pulped in machines similar to paper beaters in order to reduce the fibers to a fine state of division and to remove occluded acid. The nitrocellulose is then treated with dilute Na_2CO_3 solutions and finally washed to neutrality.

For certain industrial uses, such as the manufacture of high-grade plastics, nitrocellulose is often bleached to remove traces of color. The nitrocellulose may be bleached with a solution containing two pounds of $KMnO_4$ per 100 pounds of nitrocellulose and made slightly acid with H_2SO_4. When reduction of the permanganate is complete, the nitrocellulose is washed and the brown color removed by a solution of oxalic acid or SO_2. The nitrocellulose may also be bleached by a 30- to 60-minute treatment with a 1% solution of chlorine or bleaching powder. The nitrocellulose is then washed, treated with an antichlor, such as Na_2SO_3, to remove all traces of chlorine, and washed again.[109]

As was indicated previously, special treatment is required to produce the very low-viscosity types of nitrocellulose required for lacquers. In early industrial practice, the usual procedure[27] involved batch digestion during which nitrocellulose suspended in water was heated under pressure in welded steel, brick-lined autoclaves holding 4000 pounds of nitrocellulose and 60,000 pounds of water per charge. With digesters of this size, difficulty was sometimes encountered in removing adequately the gases resulting from the slight denitration of nitrocellulose, and explosions occurred. These explosions were probably due to the entrainment of gases in the fibrous mass, which caused dry spots in the batch. A marked advance in this phase of nitrocellulose manufacture was achieved by Milliken[27, 113] in the development of a continuous digester which avoids the hazards encountered in batch pressure digestion. In the continuous process, a suspension of purified nitrocellulose in water is fed by centrifugal pumps into a coiled, acid-resisting alloy tube 4 inches in diameter and 4000 feet long (see Fig. 7), which is heated by a steam jacket for a distance at the entrance, heat-insulated along most of its length, and cooled by a water jacket for a distance near the exit end. To prevent flashing of the water in the coil, it is subjected to a back pressure by connecting the exit to a standpipe 200 feet high. The rate of flow of the mixture and its temperature are controlled so that any practical degree of viscosity reduction can be uniformly maintained. The continuous digester is so designed that the small

[113] M. G. Milliken (to Hercules Powder Co.), U. S. Patents 1,818,733 (Aug. 11, 1931); 1,911,201 (May 30, 1933)

amounts of gas resulting from denitration move along the tube with the nitrocellulose from which they were evolved so that they have no opportunity to form gas pockets. The products of this treatment are very uniform as evidenced by their high solution clarity; their stability is also very good.

FIG. 7.—CONTINUOUS DIGESTER FOR NITROCELLULOSE VISCOSITY REDUCTION (MILLIKEN[27]).

Practically all types of nitrocellulose are dehydrated before use. The loosely held water can be removed by draining or centrifuging. The wet nitrocellulose is then transferred to hydraulic presses where it is formed into cylindrical blocks with a pressure of about 250 pounds per square inch. Denatured ethyl alcohol is then forced through the block in the proportion of about two pounds of alcohol per pound of nitrocellulose. The excess

alcohol is removed by applying a pressure of 3000 pounds per square inch to the block. The compressed block, which now contains about 30% by weight of ethyl alcohol, is broken up and packed in steel drums for shipment. Commercial nitrocellulose has also been dehydrated with isopropyl alcohol or butyl alcohol for certain uses.

(c) *Denitration of Nitrocellulose*

Although nitrocellulose is an ester, treatment of it with the usual saponification agents (aqueous alkalies) does not yield cellulose and the corresponding alkali nitrate. Instead, marked decomposition takes place with the formation of the alkali nitrite and decomposition products of cellulose. The products reported by various investigators as having been formed by the action of alkalies on nitrocellulose include inorganic nitrates and nitrites[114, 115]; ammonia[115]; cyanide[116]; carbon dioxide[117]; oxalic acid[114, 118, 119]; malic, glycolic, trihydroxyglutaric, dihydroxybutyric, malonic, and tartronic acids[118]; sugars[115, 120]; modified celluloses[115] and their nitrates[121]; partially denitrated nitrocelluloses[120, 122, 123]; and a product which is believed to be either hydroxypyruvic acid[124] ($CH_2OH \cdot CO \cdot COOH$) or 2-hydroxy-3-oxopropionic acid[125] ($CHO \cdot CHOH \cdot COOH$). Quantitative measurements have been made of the formation of nitrites[126] and of the decomposition of nitrocellulose[127, 128] as shown by alkali consumption. The most extensive quantitative investigation of the alkaline decomposition of nitrocellulose has been carried out by Kenyon and Gray,[129] who found that relatively

[114] E. Hadow, *J. Chem. Soc.*, **7**, 201 (1855).
[115] A. Béchamp, *Compt. rend.*, **41**, 817 (1855).
[116] W. Will, *Ber.*, **24**, 400 (1891).
[117] H. Vohl, *Dinglers Polytech. J.*, **112**, 236 (1849).
[118] E. Berl and A. Fodor, *Z. ges. Schiess- u. Sprengstoffw.*, **5**, 296 (1910).
[119] W. G. Mixter, *Am. Chem. J.*, **13**, 507 (1891).
[120] A. Béchamp, *Bull. soc. chim.*, [1], **3**, 289 (1863).
[121] E. Berl and A. Fodor, *Z. ges. Schiess- u. Sprengstoffw.*, **5**, 254 (1910).
[122] A. Béchamp, *Ann. chim. phys.*, [3], **46**, 338 (1856).
[123] J. M. Eder, *Ber.*, **13**, 169 (1880).
[124] J. H. Aberson, *Z. physik. Chem.*, **31**, 17 (1899).
[125] C. Neuberg and M. Silbermann, *Z. physiol. Chem.*, **44**, 134 (1905).
[126] L. Vignon and I. Bay, *Compt. rend.*, **135**, 507 (1902); T. Carlson, *Arkiv. Kemi Mineral. Geol.*, **3**, Art. 8, 1–15; *Ber.*, **40**, 4191 (1907).
[127] O. Silberrad and R. C. Farmer, *J. Chem. Soc.*, **89**, 1759 (1906).
[128] C. Piest, *Z. angew. Chem.*, **23**, 1009 (1910).
[129] W. O. Kenyon and H. Le B. Gray, *J. Am. Chem. Soc.*, **58**, 1422 (1936); this reference contains a good review of the literature on the alkaline decomposition of nitrocellulose.

small amounts of CO_2 are produced and relatively large proportions of the nitrate groups are reduced to nitrite. The production of CO_2 and reducing substances appears to be related to time, concentration of alkali, ratio of alkali to nitrocellulose, and temperature.

In attempting to explain the mechanism of alkaline decomposition of nitric acid esters, Berthelot[130] suggested that it may take place in the following way:

$$RCH_2ONO_2 + NaOH \rightarrow RCHO + NaNO_2 + H_2O \qquad (2)$$

Klason and Carlson[131] elaborated on this hypothesis and suggested that the primary products are a peroxide and a nitrite:

$$RCH_2ONO_2 + NaOH \rightarrow RCH_2OOH + NaNO_2 \qquad (3)$$

In the ordinary course of events, the peroxide will decompose into an aldehyde and water:

$$RCH_2OOH \rightarrow RCHO + H_2O \qquad (4)$$

but when a reducing agent is present, the peroxide is reduced to the alcohol.

The assumption that simultaneous oxidation and reduction take place in the treatment of nitrocellulose (and other nitric acid esters, such as nitroglycerin) with alkali, makes it easy to account for many of the products actually obtained.[132] However, Farmer[133] favors the view of Berl and Delpy[134] that the initial reaction is hydrolysis and suggests that nitric acid and the alcohol may be formed momentarily and that the alcohol is immediately oxidized by the nitric acid. It is interesting to note that Lucas and Hammett[135] recently studied the formation of benzaldehyde and sodium nitrite from benzyl nitrate in the presence of NaOH and indicated that it is premature to suggest a mechanism for this oxidation-reduction reaction.

The ability to saponify nitrocellulose to cellulose with alkalies in the presence of reducing agents has been applied commercially in the manufacture of rayon by the "nitrocellulose" process. In this process, the nitrocellulose fibers are denitrated by treatment with alkaline hydrosulfides.

Denitration of nitrocellulose also takes place on treatment with acids, but the reaction is much slower than when alkalies are used.[133] Acid denitration has been exemplified in the treatment of nitrocellulose with mixed

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[130] M. Berthelot, *Compt. rend.*, **131**, 519 (1900).
[131] P. Klason and T. Carlson, *Ber.*, **39**, 2752 (1906).
[132] T. M. Lowry, K. C. Browning, and J.-W. Farmery, *J. Chem. Soc.*, **117**, 552 (1920).
[133] R. C. Farmer, *J. Chem. Soc.*, **117**, 806 (1920).
[134] E. Berl and M. Delpy, *Ber.*, **43**, 1421 (1910).
[135] G. R. Lucas and L. P. Hammett, *J. Am. Chem. Soc.*, **64**, 1928 (1942).

acid containing more water than the acid used to produce this nitrocellulose; in this case, the esterification equilibrium shifts in the direction of lower nitrogen content. One practical aspect of this behavior was observed in the denitration of nitrocellulose which occurred while wringing out the spent acid. This denitration was caused by dilution of the spent acid with moisture from humid air; the superficial denitration which occurred decreased the solubility of the product.[136] Desmaroux[137] observed that the effectiveness of denitration of nitrocellulose with dilute solutions of HNO_3, HCl, and H_2SO_4 decreases in the order named and concluded that the denitrating action decreases with increase in size of the acid anion.

(*d*) *Constitution of Nitrocellulose*

Since the constitution of cellulose and its derivatives is discussed in Chapter II, reference will be made here only to some recent findings which deal specifically with nitrocellulose.

The degree of polymerization (that is, the number of anhydroglucose units in the molecule), determined viscometrically, of a number of nitrocelluloses was found by Staudinger and Sohn[138] to be appreciably higher than that of the original celluloses calculated from viscosity measurements in cuprammonium hydroxide solution. When the celluloses were dissolved in cuprammonium hydroxide solution, recovered by precipitation, and then nitrated, the degree of polymerization of the nitrocelluloses was the same as that of the original celluloses. According to Staudinger and Sohn, this behavior may be explained by the assumption that (A) ester linkages are formed in the cellulose chain by oxidation (particularly with acidic agents) which are stable in the nitrating acid but are readily hydrolyzed by alkali, or (B) end groups of a broken chain molecule in the cellulose fiber are condensed and linked together by the dehydrating action of the nitrating acid.

While there is no evidence showing the existence of the ester linkages suggested in hypothesis (A), there is evidence favoring the view that the viscosity behavior discussed above is due to the presence of alkali-sensitive groups in the cellulose rather than to a condensation reaction taking place during nitration. Thus, in an investigation of the oxidation of cellulose,

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[136] I. M. Naiman, N. D. Troitsky, and Ya. G. Danyushevskii, *Rev. gén. mat. plastiques*, **11**, 273, 303, 333 (1935).

[137] J. Desmaroux, *Compt. rend.*, **206**, 1483 (1938).

[138] H. Staudinger and A. W. Sohn, *Naturwissenschaften*, **27**, 548 (1939); *Ber.*, **72B**, 1709 (1939); *J. prakt. Chem.*, **155**, 177 (1940); *Melliand Textilber.*, **21**, 205 (1940); *Cellulosechem.*, **18**, 25 (1940).

Davidson[139] found that oxycellulose produced by neutral or acid oxidation suffered a loss in nitrocellulose viscosity (that is, the viscosity of a solution of nitrocellulose prepared from a given cellulose) on treatment with alkali. He suggested that certain types of oxidation do not result in direct scission of the cellulose chain molecule but produce alkali-sensitive groupings in the molecule.

An attempt has been made to determine the distribution of nitrate groups in partially nitrated cellulose based on the knowledge that sodium iodide replaces primary nitrate groups with iodine in simple sugar nitrates. The method was unsuitable for highly nitrated nitrocellulose (13.2% N) because of oxidative side reactions. On treatment of other nitrocelluloses (2.5–9.0% N) with sodium iodide, about one-half of the nitrate groups were replaced by iodine, about one-third remained unchanged, and the rest were removed. The results are taken to indicate that at least one-half of the nitrate groups in the low-substitution nitrocelluloses are in the primary position.[140]

Wide variations have been noted in the electrochemical activity of membranes prepared from commercial nitrocellulose solutions (collodion). The electrochemical activity is believed to be due to the presence in the nitrocellulose molecules of carboxyl groups which were probably formed as the result of oxidation during bleaching.[141]

(*e*) *Action of Solvents and Plasticizers on Nitrocellulose*

Solvents. The solubility of nitrocellulose in solvents is affected by many factors including the properties of the nitrocellulose (nitrogen content, viscosity, etc.), the chemical nature of the solvent, and such conditions as time and temperature. Under ordinary conditions, the nitrogen content has the greatest influence on solubility.[142, 143] Kraus[144] has determined the solubility, in a wide variety of solvents and plasticizers, of seven laboratory samples of high-viscosity nitrocellulose with N content ranging from 10.36 to 12.71% (see Table 6). More recently, the same investigator[144a] reported extensive solubility data for 14 commercial samples of nitrocellulose ranging in N content from 10.20 to 12.29% and covering the entire

[139] G. F. Davidson, *J. Textile Inst.*, **29**, T195 (1938); **31**, T81 (1940).
[140] G. E. Murray and C. B. Purves, *J. Am. Chem. Soc.*, **62**, 3194 (1940).
[141] K. Sollner, I. Abrams, and C. W. Carr, *J. Gen. Physiol.*, **24**, 467 (1941).
[142] P. Demougin, *Mém. poudres*, **26**, 37 (1934–5).
[143] M. Wadano, *Kolloid-Z.*, **93**, 324 (1940).
[144] A. Kraus, *Nitrocellulose*, **11**, 226 (1940).
[144a] A. Kraus, *Nitrocellulose*, **12**, 63 (1941).

Table 6

Solubility of Nitrocelluloses of Varied Nitrogen Content in Different Solvents and Plasticizers (Kraus[144])

Solubility Test: 0.1 g. nitrocellulose covered with 2 cc. of solvent and examined after standing 24 hours without stirring.

1 = clearly soluble
2 = almost clearly soluble
3 = slightly cloudy solution
4 = very cloudy solution
5 = extremely cloudy solution
6 = swollen
7 = not affected

Solvents	Nitrogen content in %						
	10.36	10.65	11.06	11.53	11.86	12.45	12.71
Methyl alcohol	4	3	1	1	1	4	6
Ethyl alcohol (absolute)	4	3	2	2	5	6	6
Cyclopentanol	7	7	7	7	7	6	6
Cyclohexanol	7	7	6	6	6	6	6
Diacetone alcohol	3	2	1	1	1	1	1
Benzyl alcohol	2	2	3	3	4	5	5
Methyl acetate	4	3	3	2	1	1	2
Ethyl acetate	4	4	3	2	1	1	2
Propyl acetate	3	2	2	1	1	1	2
n-Butyl acetate	4	4	3	2	1	1	1
Isobutyl acetate	4	3	1	1	1	1	1
Isoamyl acetate	5	4	2	1	1	1	1
Octyl acetate	6	5	4	2	1	1	1
Ethyl propionate	4	3	2	1	1	1	2
n-Butyl propionate	5	4	3	2	1	1	2
Isobutyl propionate	5	4	3	2	1	1	2
Amyl propionate	6	5	3	2	1	1	2
Propyl butyrate	6	4	3	2	1	1	2
Butyl butyrate	6	4	3	2	1	1	2
Amyl butyrate	6	6	5	3	2	2	2
Ethyl lactate	3	2	1	1	1	1	1
Butyl isovalerate	4	3	3	2	1	1	1
Butyl glycolate	3	2	2	1	1	1	1
Diethyl carbonate	5	4	4	3	2	2	3
Cyclohexyl acetate	4	3	2	1	1	1	1
Ethyl isobutyl ether	3	2	1	1	1	1	1
Dioxane	4	3	3	2	5	6	7
Ethylene glycol methyl ether	2	1	1	1	1	1	1
Ethylene glycol ethyl ether	2	2	1	1	1	1	1
Ethylene glycol butyl ether	3	2	2	1	1	1	1
Ethylene glycol cresyl ether	5	5	5	5	5	5	5
Ethylene glycol methyl ether acetate	2	2	1	1	1	1	1
Ethylene glycol ethyl ether acetate	3	2	1	1	1	1	2
Acetone	4	2	1	1	1	1	1
Ethyl methyl ketone	3	2	2	1	1	1	1
Cyclopentanone	2	2	1	1	1	1	3
Methyl cyclohexanone	2	1	1	1	1	1	1
Nitrobenzene	3	2	1	1	1	1	1
o-Nitrotoluene	4	3	2	1	1	1	1
n-Nitrotoluene	5	4	2	1	1	1	1
Acetic acid (glacial)	3	1	1	1	1	1	4

TABLE 6 (*Continued*)

Plasticizers	Nitrogen content in %						
	10.36	10.65	11.06	11.53	11.86	12.45	12.71
Diethyl oxalate	3	2	2	2	1	1	1
Dibutyl oxalate	5	4	3	2	1	1	1
Diamyl oxalate	7	7	4	3	2	1	1
Dimethylcyclohexyl oxalate	7	7	7	7	7	7	7
Tributyl citrate	4	3	2	1	1	1	1
Triamyl citrate	6	6	5	2	1	1	1
Dibutyl tartrate	3	2	1	1	1	1	1
Triethyl citrate	3	2	1	1	1	1	1
Ethyl sebacate	4	3	2	1	1	1	1
Dilauryl sebacate	7	7	7	7	6	6	6
Dimethyl adipate	2	1	1	1	1	1	1
Cyclohexyl adipate	7	7	6	4	3	1	2
Dimethylcyclohexyl adipate	7	7	7	6	6	4	5
Dimethylcyclohexyl methyl adipate	7	7	7	7	7	7	7
Ethyl abietate	4	4	4	3	4	4	5
Dibutyl 1,2-cyclohexanedicarboxylate	6	5	3	2	1	1	1
Methyl benzoate	1	1	1	1	1	1	1
Methyl salicylate	4	3	2	1	1	1	1
Dimethyl phthalate	2	1	1	1	1	1	1
Diethyl phthalate	3	2	1	1	1	1	1
Dibutyl phthalate	5	5	3	1	1	1	1
Diamyl phthalate	5	5	5	3	2	1	2
Benzyl butyl phthalate	6	6	5	3	2	2	2
Dilauryl phthalate	7	7	6	6	6	6	6
Bis(chloroethyl) phosphate	3	2	1	1	1	1	1
Tributyl phosphate	2	2	1	1	1	1	1
Isobutyl phosphate	3	2	2	1	1	1	1
Triamyl phosphate	5	3	2	1	1	1	1
Tricresyl phosphate	7	7	6	6	6	5	5
Methyl phthalyl ethyl glycolate	6	5	4	2	1	1	1
Butyl phthalyl butyl phthalate	6	6	5	3	2	1	1
Di(β-methoxyethyl) phthalate	2	1	1	1	1	1	1
Butyl di(β-methoxyethyl) phosphate	2	2	1	1	1	1	1
Butyl di(β-ethoxyethyl) phosphate	2	1	1	1	1	1	1
Acetophenone	1	1	1	1	1	1	1
Monoacetin	1	1	1	1	1	2	2
Diacetin	1	1	1	1	1	1	1
Triacetin	1	1	1	1	1	1	1
o(or *p*)-Toluenesulfonamide	6	6	6	6	6	6	6

viscosity range used in lacquers; in general, the lower viscosity nitrocelluloses were found to be more soluble than the high-viscosity nitrocelluloses used in the earlier study. The solubility of nitrocellulose is independent of viscosity or degree of polymerization when the latter is greater than

100–150; below this value, the solubility increases with decreasing viscosity.[143] Variation in solubility with change in physical form was shown by the observation that extraction of highly nitrated nitrocellulose with ether-alcohol resulted in only partial solution. When the fibrous residue was dissolved in acetone and recovered as a finely divided precipitate, additional material could be dissolved out with ether-alcohol.[145] The solubility of nitrocellulose (for example, in alcohol) is also dependent, in part, upon the amount of solid phase present.[146]

A study of the effect of solvent composition on the solubility of nitrocellulose showed that the solvent power of mixtures of various alcohols with ether appears to be at a maximum when the amounts of the components are equimolecular. The solvent power of hydroxy compounds was found to decrease in the following order regardless of the type of nitrocellulose: methyl, ethyl, allyl, benzyl, cyclohexyl, propyl, phenylethyl, butyl, isopropyl, isoamyl, heptyl, isobutyl, hexyl, isohexyl, octyl, and *tert*-butyl alcohols; "amylene hydrate"; *sec*-octyl alcohol; and phenol.[147]

Since the theoretical aspects of the solubility of cellulose derivatives in general will be dealt with in Chapter IX, reference will be made here only to a number of investigations dealing specifically with nitrocellulose. Trogus, Tomonari, and Hess[148] immersed nitrocellulose in binary mixtures of acetone and nonsolvents. Results of x-ray examination of the solid phase and analysis of the liquid phase led them to conclude that two loose compounds of nitrocellulose and acetone are formed which lose their acetone on exposure to the air. They suggested that a solvent for nitrocellulose must be able to form a compound with nitrocellulose and to dissolve this compound. In a binary solvent mixture, one component may form the compound and the other may dissolve it. Similar experiments with ligroin solutions of cyclohexanone, *p*-methylcyclohexanone, and fenchone indicated to these investigators that these solvents also form compounds with nitrocellulose. They made the further suggestion that compound formation between cellulose esters and organic substances follows the principles of the coordination theory, the C_6 group serving as a center at which addition occurs in the ratio 1:1 or 1:3. Trillat[149] found that freshly cast nitrocellulose films still

[145] P. Demougin, *Compt. rend.*, **196**, 408 (1933).

[146] E. v. Mühlendahl and J. Reitstötter, *Kunststoffe*, **17**, 151 (1927).

[147] J. Barbière and J. Desmaroux, *Compt. rend.*, **192**, 1231 (1931); see also, I. M. Eimont and I. A. Suirkin, *J. Applied Chem.* (*U.S.S.R.*), **8**, 322 (1934).

[148] C. Trogus, T. Tomonari, and K. Hess, *Z. physik. Chem.*, **B16**, 351 (1932); T. Tomonari, C. Trogus, and K. Hess, *Z. physik Chem.*, **B17**, 241 (1932).

[149] J. J. Trillat, *Compt. rend.*, **194**, 1922 (1932); *Trans. Faraday Soc.*, **29**, 85 (1933); *J. chim. phys.*, **31**, 125 (1934).

ontaining solvent (acetone or ethyl acetate) have a crystalline structure ifferent from that of the original nitrocellulose; on evaporation of the olvent the original crystalline structure of nitrocellulose returned. Trillat oncluded from his results that compound formation between the nitro-ellulose and solvent occurred but did not attempt to define the nature of he compound.

The interaction of solvents and nitrocellulose has been studied to some extent by observing the sorption of solvent vapors by nitrocellulose.[150] With most solvents, nitrocellulose exposed to solvent vapors at a certain temperature does not revert to its original state when the temperature is lowered; that is, sorption and desorption are not completely reversible.[151] At low relative pressures the sorption laws are followed, but as the relative pressure is raised, increased sorption causes pore formation and capillary condensation ensues. Gels were found to have more pore space than ungelatinized fibers. The predominating factor in these experiments is believed to be true adsorption.[152]

Desmaroux and Mathieu[153, 154, 155] exposed nitrocellulose to acetone vapors and observed no sign of discontinuity in the vapor sorption curve. X-ray diagrams taken during the process varied continuously with increasing acetone concentration but at no proportion of acetone did they observe the substitution of a new diagram for that of nitrocellulose. They concluded from these results that acetone combines regularly with nitrocellulose throughout the sorption process by forming a solid solution. The acetone molecules lodge in the plane of the anhydroglucose rings and cause the nitrocellulose chains to spread apart until a maximum distance is reached at which one mole of acetone is fixed for each C_6 group. Further sorption occurs without change of space until gelatinization takes place when the number of fixed acetone molecules is equal to the number of NO_2 groups; at this point the crystal structure becomes disorganized. Behavior similar to that described above was also observed with cyclopentanone and methyl nitrate.[156] Desmaroux and Mathieu[155] believe

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[150] W. J. Jenkins and H. B. Bennett, *J. Phys. Chem.*, **34**, 2318 (1930).

[151] L. Rubenstein, *J. Phys. Chem.*, **34**, 2330 (1930).

[152] J. W. McBain, S. J. Good, A. M. Bakr, D. P. Davies, H. J. Willavoys, and R. Buckingham, *Trans. Faraday Soc.*, **29**, 1086 (1933).

[153] M. Mathieu, *Trans. Faraday Soc.*, **29**, 122 (1933).

[154] M. Mathieu, *La Gélatinisation des Nitrocelluloses—Réaction Topochimique*. Hermann & Cie., Paris, 1936.

[155] J. Desmaroux and M. Mathieu, *Mém. poudres*, **26**, 180 (1934–5).

[156] J. Desmaroux, M. Mathieu, and T. Petitpas, *Mém. poudres*, **28**, 204 (1938); T. Petitpas, *J. chim. phys.*, **37**, 6 (1940).

that their results fail to indicate formation of the compounds postulated by Trogus, Tomonari, and Hess.[148]

Kanamaru and coworkers[157–162] have carried out an extensive series of investigations of the electrical phenomena occurring at the interface between nitrocellulose (and other cellulose derivatives) and organic liquids and have concluded that there is a close relation between zeta-potential and solubility.

Lee and Sakurada[163] calculated the apparent specific polarization of nitrocelluloses from the dielectric constant of their solutions. The apparent specific polarization of nitrocellulose was only slightly dependent on viscosity or nitrogen content; it was practically independent of nitrocellulose concentration in acetone and ethyl acetate solutions but varied with nitrocellulose concentration in acetone-hexane solutions. The authors concluded that nitrocellulose is so strongly solvated in strongly polar solvents (acetone, ethyl acetate) that dipole association and change in solvation do not take place within a large range of nitrocellulose concentration.

Nitrocellulose has a positive heat of solution. Treatment of nitrocellulose with benzene-acetone mixtures results in the liberation of a relatively large amount of heat at low acetone concentrations where little solution occurs; it is believed that this heat is mainly heat of solvation.[164] Experiments by Okatov and Emmanuilova[165] on the interaction of nitrocellulose and ether-alcohol mixtures indicate that the following stages are passed through: wetting, solvate formation, swelling, and solution. If solvate formation is limited, then swelling is limited. The heat of wetting of nitrocellulose with ether-alcohol mixtures was greatest with a 1:1 mix-

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[157] K. Kanamaru and J. Chao, *J. Soc. Chem. Ind., Japan*, **41**, suppl. binding, 171 (1938).

[158] K. Kanamaru and T. Kohno, *Kolloid-Z.*, **79**, 190, 198 (1937); *J. Soc. Chem. Ind., Japan*, **40**, suppl. binding, 102, 128 (1937).

[159] K. Kanamaru and T. Takada, *Kolloid-Z.*, **90**, 315 (1940); *Z. physik. Chem.*, **A186**, 10 (1940).

[160] K. Kanamaru, T. Takada, and K. Maeda, *J. Soc. Chem. Ind., Japan*, **41**, suppl. binding, 153 (1938); *Z. physik. Chem.*, **A182**, 278 (1938).

[161] K. Kanamaru, T. Takada, and E. Wada, *Kolloid-Z.*, **90**, 183 (1940).

[162] K. Kanamaru and S. Ueno, *Kolloid-Z.*, **79**, 77 (1937); *J. Soc. Chem. Ind., Japan*, **40**, suppl. binding, 91 (1937).

[163] S. Lee and I. Sakurada, *Kolloid-Z.*, **82**, 194 (1938); *J. Soc. Chem. Ind., Japan*, **40**, suppl. binding, 460 (1937).

[164] T. Nakashima and N. Saito, *J. Soc. Chem. Ind., Japan*, **38**, suppl. binding, 232 (1935).

[165] A. P. Okatov and Z. I. Emmanuilova, *J. Applied Chem.* (*U.S.S.R.*), **8**, 1248 (1935).

ure and smallest with ether alone. As expected from thermodynamic considerations, swelling and solution formation were accelerated by lowering temperature and increasing pressure. Berl and Koerber[166] observed that nonsolvents for nitrocellulose at room temperature may become solvents at low temperatures (−50°C.) and explained this behavior by the formation of soluble molecular compounds which are not stable at ordinary temperature and by the exothermic nature of the swelling reaction.

Plasticizers. The combination of nitrocellulose with camphor, which is commonly known as celluloid, is the oldest of the synthetic plastics. Since the discovery of celluloid about seventy years ago, many compounds have been examined as possible substitutes for camphor, but none of these have succeeded in producing a plastic with nitrocellulose fully equal to celluloid. For this reason, camphor has often been called the perfect plasticizer.

Investigations have been carried out, using a variety of experimental methods, to determine the fundamental nature of the relation between camphor and nitrocellulose in celluloid. Thus, it was found that camphor is absorbed by nitrocellulose from solution in a saturated hydrocarbon solvent only above a certain critical concentration of camphor.[167] A study of the effect of camphor content on the rate of elongation of celluloid films under static stress showed that a discontinuity in the elongation-camphor content curve is obtained at 35% camphor content.[168] These results, as well as those obtained from double refraction and x-ray measurements and from chemical examination of various mixtures of camphor and nitrocellulose, indicate that a camphor-nitrocellulose compound is formed containing at least one mole of camphor for each C_6 group in the nitrocellulose.[169–172] Trillat[173] calls the camphor-nitrocellulose complex a solvate and suggests that the action of plasticizers is due to saturation of

[166] E. Berl and W. Koerber, *J. Am. Chem. Soc.*, **61**, 154 (1939); see also J. B. Bernadou, *Smokeless Powder, Nitrocellulose and the Theory of the Cellulose Molecule.* John Wiley, New York, 1908, p. 52 *et seq.*

[167] J. Desmaroux, *Mém. poudres*, **23**, 54 (1928).

[168] J. G. McNally and S. E. Sheppard, *J. Phys. Chem.*, **35**, 2498 (1931); see also M. Wadano, *Kolloid-Z.*, **93**, 103 (1940).

[169] J. C. Derksen, J. R. Katz, K. Hess, and C. Trogus, *Z. physik. Chem.*, **A149**, 371 (1930).

[170] J. R. Katz, J. C. Derksen, C. A. Kramers, K. Hess, and C. Trogus, *Z. physik. Chem.*, **A151**, 145 (1930).

[171] K. Hess, T. Tomonari, and C. Trogus, *Z. physik. Chem* , **B16**, 374 (1932).

[172] See also M. Wadano, K. Hess, and C. Trogus, *Z. physik. Chem.*, **B30**, 159, 183, 232 (1935).

[173] J. J. Trillat, *Compt. rend.*, **191**, 654 (1930).

the lateral forces of attraction between the primary valence chains resulting in easier slipping between these chains. McNally and Sheppard[168] pointed out that the ease with which camphor can be removed from celluloid indicates that the camphor-nitrocellulose complex must be unstable; below 35% camphor, celluloid consists of a mixture of nitrocellulose and the complex, while above 35% camphor the components are camphor and the complex.

X-ray examination and double refraction measurements have indicated that compound formation also takes place between nitrocellulose and the following plasticizers: fenchone, menthone, carvone, cyclopentanone, cyclohexanone, cyclohexanol, diethyldiphenylurea, ethylacetanilide, dimethyl phthalate, and triisoamyl phosphate. Since ketones, amides, and esters all have the carbonyl group in common, it has been suggested that compound formation takes place through the latent valences of this group.[174]

(*f*) *Nitrocellulose Solutions*

Viscosity. Since the general aspects of viscosity will be dealt with in Chapter IX, reference will be made here only to a number of investigations on viscosity changes which occur in nitrocellulose solutions. The variation of the viscosity of nitrocellulose solutions with change in concentration is expressed graphically in Figure 8.

Electrolytes exert important effects on the viscosity of nitrocellulose solutions. As the content of alkaline earth hydroxides (especially $Ca(OH)_2$) in concentrated nitrocellulose solutions increases, there is also a large increase in viscosity[176]; the viscosity of dilute solutions remains unchanged. Electrodialysis,[177] boiling in distilled water, or treatment with a solution of sodium hexametaphosphate,[178] all lower the viscosity of nitrocellulose in concentrated solution. Addition of HCl to lime-containing nitrocellulose solutions causes an immediate viscosity reduction; Rogovin and Shlyakhover[179] suggest that a nitrocellulose–$Ca(OH)_2$ complex is formed which increases the aggregation of particles in solution. Since

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[174] J. R. Katz, J. C. Derksen, K. Hess, and C. Trogus, *Z. physik. Chem.*, **A151**, 163, 172 (1930).

[175] *Nitrocellulose.* Hercules Powder Co., Wilmington, Del., 1939.

[176] S. A. Glikman, S. S. Mindlin, V. Guseva, and P. Zel'dovich, *Plasticheskie Massy*, **1933**, No. 4, 11; S. A. Glikman, *J. Phys. Chem.* (*U.S.S.R.*), **11**, 512 (1938).

[177] V. A. Kargin and E. Ya. Vinetskaya, *J. Phys. Chem.* (*U.S.S.R.*), **10**, 788 (1937).

[178] A. Pakshver, S. Frolov, and L. Lebedeva, *Trans. Inst. Chem. Tech. Ivanovo* (*U.S.S.R.*), **1940**, No. 3, 165.

[179] Z. A. Rogovin and M. Shlyakhover, *Kolloid-Z.*, **78**, 224 (1937)

HCl has no effect in lime-free solutions, they believe that the HCl destroys the nitrocellulose-lime complex.

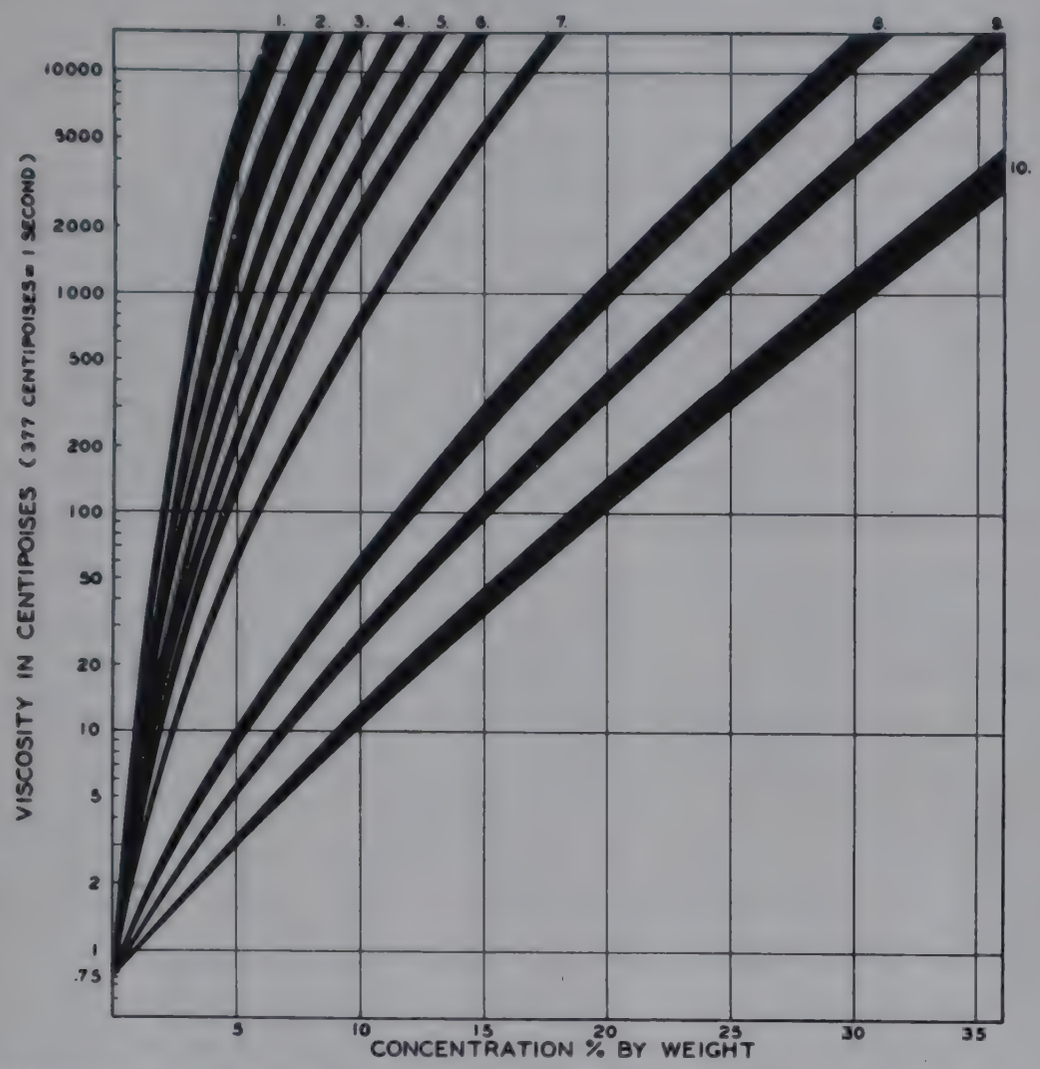

FIG. 8.—VISCOSITY–CONCENTRATION CURVES FOR HERCULES NITROCELLULOSES[175] (11.8–12.2% N; Solvent: 75:25 butyl acetate:ethanol, by weight.)

Curve	Standard viscosity type	Curve	Standard viscosity type
1	600–1000 sec.	6	15–20 sec.
2	250– 400 sec.	7	5– 6 sec.
3	125– 175 sec.	8	1/2 sec.
4	60– 80 sec.	9	1/4 sec.
5	30– 40 sec.	10	18–23 cps.

The viscosity of nitrocellulose solutions usually decreases on aging[180]; this viscosity decrease is accelerated by exposure to light.[181] Drinberg[182]

[180] L. Medard, *Mém. poudres*, **26**, 123 (1934–5).
[181] Z. A. Rogovin and S. Glazman, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 498 (1938).
[182] A. Y. Drinberg. *J. Applied Chem.* (*U.S.S.R.*), **4**, 293 (1931).

attributes the decrease in viscosity and in degree of polymerization to th influence of electrolytes, while Grévy[183] has obtained evidence showing tha the viscosity decrease of nitrocellulose solutions stored in glass is due, a least in part, to alkali from the glass.

Wehr[184] observed that the viscosity decrease on aging is independen of the concentration and of the solvent, provided that the latter is pur The degradation, as measured by decrease in degree of polymerization, independent of the original degree of polymerization. Viscosity drop accelerated by acids and oxygen and is slowed down by antioxidants.

Coagulation. Nitrocellulose solutions may be coagulated by the addi tion of nonsolvents or of suitable electrolytes. The addition of finel ground PbO, CaO, or $Ca(OH)_2$ to a 1% solution of nitrocellulose in aceton alcohol-ether, or amyl acetate causes first an increase in viscosity and the gelation.[185] Nitrocellulose solutions can be coagulated in the presence o small amounts of alkali by boric acid and certain metal oxides. Wit the oxides of Mn, Fe, Ni, Cu, and Zn, the resultant gel passes into a solu tion on standing; with Pb or Al oxides, syneresis of the gel occurs.[186] Ex periments on the coagulation of acetone solutions of nitrocellulose by th addition of water and aqueous solutions of $ZnSO_4$, $MgCl_2$, and AlC indicate that the particles in nitrocellulose organosols carry little or n electrical charge.[187] Addition of small amounts of bronzing powders an copper salts to nitrocellulose solutions produce clear, green, solid gels Gloor and Spurlin[188] suggest that a combination between Cu and reduce nitrate groups is formed as the result of secondary valence forces. Th higher the molecular weight of the nitrocellulose, the smaller is the amoun of gelling agent required to produce a strong gel. A study of the effec of metals and their salts on the viscosity of nitrocellulose solutions showe that stabilization increases the time required for gelation to occur; nitri acid and nitrogen oxides accelerate the gelation.[189] The gelation of a so containing nitrocellulose, antimony oxide, or titanium oxide, and diglyco laurate in butyl acetate-alcohol is attributed by de Waele[190] to reactio between the pigment and carboxyl groups formed in the nitrocellulose b

[183] J. Grévy, *Compt. rend.*, **202**, 480 (1935).
[184] W. Wehr, *Kolloid-Z.*, **88**, 185, 290 (1939).
[185] A. Apard, *Compt. rend.*, **186**, 153 (1928).
[186] I. R. Morozov, *J. Chem. Ind.* (*U.S.S.R.*), **8**, 863 (1931).
[187] S. Papkov and M. Chveleva, *Kolloid-Z.*, **73**, 202 (1935).
[188] W. E. Gloor and H. M. Spurlin, *J. Am. Chem. Soc.*, **58**, 854 (1936).
[189] A. V. Pamfilov, A. G. Shikher, and M. G. Shikher, *Colloid J.* (*U.S.S.R.*), **4**, 56 (1938); A. V. Pamfilov and M. G. Shikher, *Colloid J.* (*U.S.S.R.*), **4**, 587 (1938).
[190] A. de Waele, *J. Oil Colour Chem. Assoc.*, **22**, 65 (1939).

xidation; the reaction causes tridimensional linkage between emulsoid itrocellulose particles. According to Vodyakov,[191] the amount of metal n nitrocellulose gels, obtained by absorption of metallic oxides or hyroxides or by electrolysis of an acetone solution of nitrocellulose, is approximately proportional to the nitrogen content of the nitrocellulose.

2. Cellulose Sulfate

The ability of concentrated sulfuric acid (preferably about 72% strength) o dissolve cellulose has been known for over a century. If the cellulose s precipitated immediately after dissolving, it contains little or no combined sulfate. Esterification will take place if the cellulose is left in solution for a time. Reference has already been made to the formation of nixed sulfuric-nitric acid esters of cellulose during nitration with H_2SO_4—HNO_3 mixtures.

Braconnot[192] reported in 1819 that linen dissolves in cold concentrated ulfuric acid and that on dilution with water a clear solution is obtained vhich contains, in addition to H_2SO_4, another acid which he called "*acide égéto sulphurique.*" The barium salt of this acid, which remained in olution, could be precipitated by addition of alcohol. Analysis of the alt by de Carolles[193] showed that the amount of Ba combined with the ellulose increased with time of contact between the concentrated H_2SO_4 nd the cellulose; the product obtained after the solution was allowed to tand for 24 hours before dilution was reported to have a composition orresponding to $C_4H_8O_4(SO_3)_2BaO \cdot 2H_2O$. A barium salt[194] with the omposition $C_{90}H_{180}O_{90}BaO(SO_3)_2$ and a lime salt[195] corresponding to $C_{33}H_{28}O_8(SO_3)_2CaO$ have also been reported.

Hönig and Schubert[196] dissolved cellulose in concentrated H_2SO_4 at room emperature and prepared Cu, Pb, and Ba salts of the cellulose sulfate. They confirmed de Carolles' observation that the ratio of Ba to H_2SO_4 in the salts is always 1:2. Stern[197] neutralized a sulfuric acid solution of cellulose with baryta and decanted the clear liquid after $BaSO_4$ had settled out. He concentrated the clear liquid on a water bath and then under vacuum; the solution remained neutral. The Ba salt was precipitated

[191] L. T. Vodyakov, *Trans. Kirov Inst. Chem. Tech. Kazan*, **1940**, No. 8, 61.
[192] H. Braconnot, *Ann. chim. phys.*, [2], **12**, 185 (1819).
[193] B. de Carolles, *Ann.*, **52**, 412 (1844).
[194] H. Fehling, *Ann.*, **53**, 135 (1845).
[195] R. Marchand, *J. prakt. Chem.*, **35**, 199 (1845).
[196] M. Hönig and S. Schubert, *Monatsh.*, **6**, 708 (1885).
[197] A. L. Stern, *J. Chem. Soc.*, **67**, 74 (1895).

by adding alcohol, and after purification and drying, was obtained in 48% yield as a white hygroscopic powder with a composition corresponding to $C_6H_8O_3(SO_4)_2Ba$.

Traube,[198] Blaser, and Grunert[199] found that well-dried cellulose combines with SO_3 vapors without charring to form cellulose trisulfate; the formation of lower sulfates could not be detected. When sufficient SO_3 had been added for complete esterification, the product was dissolved in water and treated with a slight excess of $PbCO_3$. After removal of the Pb with H_2S, the product was neutralized with KOH. On cooling the solution, separation of "potassium cellulose trisulfate A" occurred; this product, which was obtained in 65% yield, had a composition corresponding to $C_6H_7O_5(SO_3K)_3$. Concentration of the mother liquor yielded more material of the same composition but with different specific rotation.

Gebauer-Fülnegg,[200] Stevens, and Dingler[201] esterified cellulose with a mixture of chlorosulfonic acid ($ClSO_3H$) and pyridine at 100°C. until complete solution occurred. On addition of alcohol, the pyridine salt was precipitated; with alcohol containing NaOH or NaCl, the sodium salt was obtained. Addition of Ba salts to solutions of the other salts yielded a Ba salt of the cellulose sulfate which was insoluble in water and very resistant to acid hydrolysis. Analysis showed that the products prepared by this process were almost completely esterified; that is, the substitution was nearly 3.0. In order to determine the extent of degradation that had occurred in the esterification, they investigated methods for removing the sulfate without excessive decomposition. This was finally accomplished by treating the cellulose sulfate with methanol containing 0.5% hydrochloric acid for six hours under reflux. The regenerated, sulfur-free cellulose showed a specific rotation in cuprammonium hydroxide solution similar to that of native cellulose. It could also be converted to trimethylcellulose and cellulose triacetate.[202] However, no data indicative of molecular weight were presented to prove that the product had not been strongly degraded.

Traube and coworkers[203] studied the $ClSO_3H$-pyridine esterification process and found that the product ordinarily obtained had a substitution of about 2.6; prolonged esterification yielded a product with substitution

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[198] W. Traube, French Patent 657,204 (Jan. 11, 1929).
[199] W. Traube, B. Blaser, and C. Grunert, *Ber.*, **61B**, 754 (1928).
[200] E. Gebauer-Fülnegg, U. S. Patent 1,734,291 (Nov. 5, 1929).
[201] E. Gebauer-Fülnegg, W. H. Stevens, and O. Dingler, *Ber.*, **61B**, 2000 (1928).
[202] E. Gebauer-Fülnegg and O. Dingler, *J. Am. Chem. Soc.*, **52**, 2849 (1930).
[203] W. Traube, B. Blaser, and E. Lindemann, *Ber.*, **65B**, 603 (1932).

of 2.9. Further investigation of their own process showed that it is advantageous to use a carbon disulfide solution of SO_3 in place of gaseous SO_3 and to have an excess of cellulose present. The reaction mixture is worked up by pouring it into an excess of KOH solution, filtering off the unesterified cellulose, and recovering the potassium cellulose trisulfate as before. The viscosity of a 1% aqueous solution of sodium cellulose sulfate (substitution 2.6) prepared by the $ClSO_3H$-pyridine method was found to be much higher than that of a similar solution of potassium cellulose trisulfate prepared by the SO_3 process. This was taken to indicate that appreciable depolymerization had taken place in the latter case. Hagedorn and Guehring[204] have claimed the preparation of cellulose sulfate by reacting alkali cellulose with an oxygen-containing chloride of sulfuric acid (for example, SO_2Cl_2) in presence of benzene. Schulze[205] has patented the preparation of cellulose sulfate by treatment of cellulose with SO_3 in presence of a tertiary amine such as pyridine. Rigby esterified cellulose with (a) pyrosulfuric acid ($H_2S_2O_7$) or its equivalent in the presence of a tertiary amine like pyridine,[206] and (b) a mixture of a substance containing the radical $-O-SO_2$ (for example, chlorosulfonic acid), a tertiary amine, and an inert diluent (for example, toluene).[207] Rubenstein[208] prepared cellulose sulfate insoluble in water but soluble in cold dilute NaOH solution by treating cellulose with up to one-half mole of a sulfating agent in presence of NaOH or a tertiary cyclic amine.

Caille[209] treated strips of cotton cloth with a mixture of equal parts of H_2SO_4 and acetic acid at 45°C. for 30 minutes. The product, which retained its original fibrous structure, could be washed neutral with alcohol or calcareous water; washing with ordinary water caused hydrolysis. Heat tests showed that the stability of the product increases with increasing neutralization of the combined acid groups by the alkaline constituents of the wash water. The cotton cloth had an affinity for basic dyes. Numerous patents have been granted covering superficial treatments of cellulose with compounds of sulfur to change its dyeing properties and its resistance to water.[210]

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[204] M. Hagedorn and E. Guehring, U. S. Patent 1,848,524 (Mar. 8, 1932).
[205] F. Schulze, U. S. Patent 2,016,299 (Oct. 8, 1935).
[206] G. W. Rigby, U. S. Patent 2,025,073 (Dec. 24, 1935).
[207] G. W. Rigby, U. S. Patent 2,033,787 (Mar. 10, 1936).
[208] L. Rubenstein, U. S. Patent 2,042,484 (June 2, 1936).
[209] A. Caille, *Chimie & industrie*, **15**, 189 (1926).
[210] O. Faust, *Celluloseverbindungen*, p. 518; see ref. 1, p. 622.

3. Cellulose Phosphate

Champetier[211] has reported the formation of an addition compound having the composition $3C_6H_{10}O_5 \cdot H_3PO_4$ on treatment of cellulose with aqueous phosphoric acid solutions. The addition compound was destroyed by washing with water; the fibrous cellulose was recovered apparently unchanged. Cellulose phosphate (containing about 16% PO_4) has been prepared by treating cellulose with an oxygen-containing chloride of phosphoric acid in the presence of benzene.[204] Tanner[212] has prepared a product containing about 17% phosphorus (cellulose triphosphate would have 23% P) by treating cellulose with a mixture containing concentrated sulfuric and phosphoric acids and a small amount of a weak acid catalyst (for example, glacial acetic, boric, or formic acids). Cellulose phosphate may be prepared by treating cellulose with moderately concentrated phosphoric acid and $POCl_3$ with or without the addition of a diluent.[213] In a modification of this process, cellulose is treated with concentrated phosphoric acid and a small amount of another inorganic acid (for example, H_2SO_4); the cellulose ester is precipitated by addition of water to the reaction mixture.[214] Patents have also been issued covering the modification of the dyeing and other properties of cellulose by superficial treatment with a variety of phosphorus compounds.[210]

4. Cellulose Esters of Other Inorganic Acids

Treatment of cotton with thionyl chloride ($SOCl_2$) in presence of pyridine resulted in the introduction of one atom of chlorine for each $C_6H_{10}O_5$ group; the reaction product was dark in color and almost a powder.[215] An attempt has been made to esterify cellulose by dissolving it in fluorosulfonic acid (FSO_3H), but results on identification of the cellulose ester formed are inconclusive.[216] A cellulose derivative containing sulfur was prepared by treating hydrocellulose with sulfur monochloride in hydrochloric acid.[217]

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[211] G. Champetier, *Compt. rend.*, **196,** 930 (1933); *Ann. chim.*, [10], **20,** 5 (1933).
[212] W. L. Tanner, U. S. Patent 1,896,725 (Feb. 7, 1933).
[213] I. G. Farbenindustrie Akt.-Ges., German Patent 547,812 (Mar. 29, 1932).
[214] I. G. Farbenindustrie Akt.-Ges., German Patent 556,590 (Aug. 17, 1932).
[215] P. Carré and P. Mauclère, *Compt. rend.*, **192,** 1567 (1931).
[216] C. H. Möllering, *J. prakt. Chem.*, **134,** 209 (1932).
[217] R. Sthamer, German Patent 137,206 (Dec. 2. 1902).

C. CELLULOSE ORGANIC ACID ESTERS

CARL J. MALM AND CHARLES R. FORDYCE

Cellulose as a polyhydroxy alcohol offers the possibility of ester formation with any organic acid. The complexity of the cellulose molecule, however, makes it difficult to obtain a high degree of esterification with many acids, and also limits the variety of reaction methods which can be successfully applied. For these reasons, although cellulose derivatives esterified with minor quantities of a great many organic acids have been prepared, those of a high degree of esterification have been confined quite largely to the normal fatty acid series and to the simpler aromatic acids.

Derivatives of cellulose are usually prepared with the objective of obtaining physical properties not presented by cellulose itself. Treatments which result in only slightly modified cellulose, yielding no soluble derivatives or no greatly changed physical properties, are therefore of comparatively minor interest. It is also important that the derivative be obtained under conditions which preserve the high molecular structure of the cellulose chain, otherwise the product will represent not cellulose, but rather a degraded carbohydrate derivative.

Methods for preparation of cellulose esters may in general be classified as esterification by reaction of (1) acids, (2) anhydrides, and (3) acid chlorides.

Appreciable esterification by direct treatment of cellulose with an organic acid is possible only in the case of the formate.[1] Room temperature treatment of cellulose with formic acid results in introduction of a small amount of formyl, and by addition of an acid catalyst this may be increased to a sufficiently high degree of esterification to produce soluble products.

Other organic acids at room temperature yield practically no esterification of cellulose. Clarke and Malm[2] have shown that acetic, propionic, and butyric acids at their boiling points produce minor degrees of esterification, the exact extent depending upon the reactivity of the cellulose. Treatment with higher acids, hot or cold, results in only low degrees of re-

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[1] I. Sakurada, *J. Soc. Chem. Ind., Japan*, **35**, B123 (1932).

[2] H. T. Clarke and C. J. Malm, *J. Am. Chem. Soc.*, **51**, 274 (1929).

action. The use of catalysts to promote reaction under these conditions usually results in severe degradation and has not been a useful esterification procedure.

An indirect process involving the use of substituted anhydrides, which in themselves do not esterify cellulose, as impelling agents to bring about reaction has been found to have wide applicability and may be used as a general method of esterification, particularly with high-molecular-weight acids. As impelling agents, anhydrides of halogen[3, 4] or alkoxy-substituted[5] acetic acid are effective, monochloroacetic anhydride being the most useful material for general application. A reaction mixture of 1 part of cellulose with 5 parts of chloroacetic anhydride, 0.2 part of magnesium perchlorate as catalyst, and slightly more than the calculated amount of the acid to be esterified may be reacted at 60–70°C., resulting in a solution of the cellulose ester within a period of a few hours.

The impelling agent in this process brings about conversion of the esterification acid to its anhydride. The reaction is thus an esterification by anhydride, but it is only necessary to use the calculated amount of acyl to react with the cellulose, whereas usual anhydride reactions require at least double that amount. These acids are frequently poor solvents for the reaction product, and they are undesirable components of a reaction mixture.

Esterification by acid anhydrides in the presence of mineral acid catalysts is probably the most widely known process of esterification because of its commercial use for cellulose acetate manufacture. The same general process may be made to operate with propionic and butyric anhydrides, but, for either aliphatic or aromatic anhydrides of higher molecular weight, reactivity is not sufficient to produce high degrees of esterification. Soluble cellulose derivatives containing free hydroxyl groups, such as acetone-soluble cellulose acetate, may, however, be treated with higher anhydrides in the presence of acid catalysts to esterify the free hydroxyl groups and yield mixed esters.

Tertiary organic bases such as pyridine may be used as reaction media for organic anhydrides, but, even at reflux temperatures, the activity is not sufficient to produce complete esterification, except for special cases such as the action of acetic anhydride on exceptionally reactive forms of cellulose. This type of reaction is, therefore, generally useful only for partial

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[3] H. T. Clarke and C. J. Malm, U. S. Patent 1,880,808 (Oct. 4, 1932); Brit. Patent 313,408 (Aug. 27, 1929).

[4] I. G. Farbenindustrie Akt.-Ges., German Patent 516,250 (Jan. 20, 1931).

[5] H. T. Clarke and C. J. Malm, U. S. Patent 1,987,053 (Jan. 8, 1935).

esterification. Use of pyridine hydrochloride as a reaction medium for anhydrides provides a much stronger reaction condition.[6] This may be explained by formation of acid chlorides as the effective esterification agents.

Acid chlorides of nearly all types of organic acids may be depended upon to react with cellulose in the presence of pyridine as a reaction medium. It is necessary to employ a large excess of acid chloride to obtain complete esterification, especially with acids of high molecular weight. The reaction is carried out at elevated temperatures, usually from 60 to 100°C. In certain cases, such as with acetyl chloride and toluenesulfonyl chloride, secondary reactions result in appreciable quantities of combined nitrogen and chlorine in the cellulose derivative, making special precautions necessary.

Aromatic and high-molecular-weight aliphatic acid chlorides have been reacted with alkali cellulose to produce partial esterification. Under these conditions it is also necessary to employ excessive amounts of reagent, and the process is, in general, inferior to the pyridine reaction.

As starting materials for cellulose ester preparation, various types of cellulose have been employed, that most commonly used being bleached and purified cotton linters. As a by-product of the cotton industry, this material has been available at reasonable prices and of quality satisfactory for chemical use. The viscosity of solutions of native cotton linters is higher than necessary for esterification and may be adjusted during purification to a suitable value which may vary according to the esterification process to be used. Analytical characteristics typical of cotton linters suitable for acetylation are as follows:

Alpha-cellulose	99%
Solubility in 7.14% NaOH	1.8%
Pentosans	0.8%
Ash	0.08%

Purified wood cellulose may also be employed in esterification processes if properly treated to yield a quality approaching that of cotton linters, at the same time preserving uniform chemical reactivity and sufficient viscosity so that esterification conditions would not reduce it to too low a figure. Care should be taken to make sure that conditions of bleaching during purification have not resulted in harmful oxidation of the cellulose.

For preparations of special cellulose esters and, to a considerable extent

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[6] J. F. Haskins and F. Schulze, U. S. Patent 1,967,405 (July 24, 1934).

in experimental investigations, chemically modified celluloses have been used as starting materials because of their increased chemical activity as compared with native celluloses.

Cellulose regenerated from cuprammonium or viscose solutions provides a useful source of raw material lower in viscosity than the native celluloses, and useful for mild reaction conditions. Another form of cellulose very useful for experimental study is that regenerated from acetone-soluble cellulose acetate by suspension of the material in aqueous ammonia (15%) for a period of two or three days to bring about complete deacetylation. This cellulose has the advantage that it has the chain length of a typical cellulose ester, and can be esterified under mild experimental conditions to produce soluble derivatives.

1. Aliphatic Fatty Acid Esters

(*a*) *Cellulose Formate*

Cellulose formates have been of little interest, either for theoretical study or for commercial use, because of their instability. They are hydrolyzed readily by hot water, and they show a strong tendency toward development of acidity at room temperature in the presence of moisture. Furthermore, the formyl groups are removed completely by dry heating at elevated temperatures, and cellulose is regenerated on such a treatment.[7]

Complete esterification with formic acid is very difficult to obtain, although it is claimed that the triformate can be made using zinc chloride as a catalyst.[8] The usual reaction products contain 20–30% formyl, corresponding to approximately a diformate.[9,10,11] To obtain these products, the use of swelling agents such as $ZnCl_2$ or $CaBr_2$ and of catalysts such as HCl gas, sulfuric acid, and P_2O_5 are recommended, and metal perchlorates, especially magnesium perchlorate, are said to have catalytic activity.[12] The temperature used varies with the catalysts employed, but, to prevent degradation of the cellulose, Elöd[10] and Jurling[13] recommended tempera-

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[7] G. Tocco, *Giorn. chim. ind. applicata*, **13**, 325, 414 (1931).

[8] I. G. Farbenindustrie Akt.-Ges., German Patent 636,307 (Dec. 18, 1930).

[9] Y. Ueda, S. Nakamura, and T. Shimada, *Cellulose Ind.* (Tokyo), **15**, 212 (1939); references to earlier papers are included.

[10] E. Elöd, U. S. Patent 1,900,599 (Mar. 7, 1933); British Patent 275,641 (Aug. 9, 1926); French Patent 638,431 (Aug. 29, 1927); German Patent 528,148 (June 25, 1931).

[11] R. Koepp & Co. Chemische Fabrik A.-G., German Patent 657,874 (Mar. 16, 1938).

[12] A. Dobry, French Patent 780,775 (May 3, 1935).

[13] J. G. Jurling, U. S. Patent 1,656,119 (Jan. 10, 1928).

tures of 5°C. and below. The physical properties of films and filaments made from these formates have been investigated by Ueda.[14]

The formation of cellulose formate containing low percentages of formyl groups is said to be useful as a means of activating cellulose for further esterification with other acids.[15] These formates have 6–10% formyl and are easily made by soaking the cellulose at room temperature in formic acid of at least 85% strength. Commercial use of such products, however, is negligible.

(*b*) *Cellulose Acetate*

Cellulose acetate is the most widely known of organic cellulose derivatives. It is at the present time made in large commercial quantities for a variety of uses including the manufacture of cellulose acetate rayon, photographic films and other forms of transparent and pigmented sheeting, plastic compositions such as those used for compression and injection molding, and, to a more limited extent, surface coatings. Annual production of cellulose acetate in the United States has increased rapidly during the past fifteen years, as shown in the curve of Figure 9, plotted from estimated data. The product used is almost exclusively acetone-soluble acetate made by partial hydrolysis of the triester, as first described by Miles in 1905.[16] It is common practice today to refer to the fully esterified ester as the triacetate or primary acetate and to the hydrolyzed product as acetone-soluble or secondary acetate.

The most outstanding technical developments within recent years have been in the direction of greatly reduced cost of manufacture, of improved control of processing conditions, resulting in better clarity and uniformity of product, and of development of mild conditions of acetylation to prevent excessive degradation of the cellulose, retaining the high molecular structure of the cellulose molecule which contributes to the strength and durability of the product.

A continual trend toward milder esterification conditions has been noticeable throughout the history of cellulose acetate. The first reported acetylation of cellulose was accomplished by Schützenberger in 1865[17] by the action

[14] Y. Ueda and T. Shimada, *Cellulose Ind.* (Tokyo), **15**, 426 (1939); references to earlier papers are included.

[15] P. A. Chevalet, Brit. Patent 264,181 (Jan. 11, 1926); H. Dreyfus, French Patent 642,329 (Sept. 16, 1927); H. Dreyfus and C. Haney, Brit. Patent 288,657 (Apr. 10, 1928); I. G. Farbenindustrie Akt.-Ges., Brit. Patent 305,601 (Feb. 5, 1929); R. O. Herzog and G. Frank, French Patent 700,165 (Aug. 7, 1930).

[16] G. Miles, French Patent 358,079 (Dec. 5, 1905).

[17] P. Schützenberger, *Compt. rend.*, **61**, 485 (1865).

of acetic anhydride in a sealed tube at 180°C. The amorphous powder which resulted was soluble in alcohol. Franchimont in 1879[18] used various catalysts to improve the esterification reaction and obtained two types of products distinguished by their solubility in hot or cold alcohol. Later investigations, including those of Cross and Bevan and Miles during the period 1900–1905, still employed comparatively high acetylation tempera-

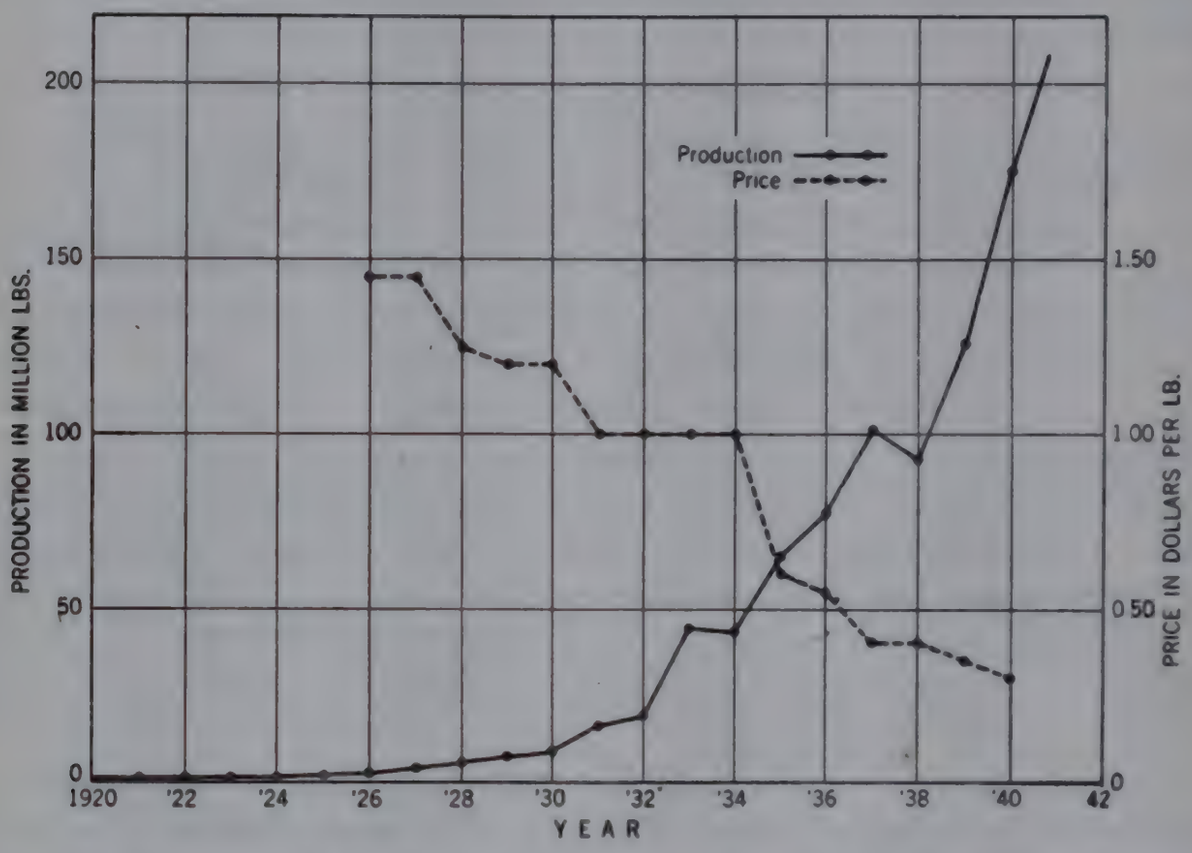

FIG. 9.—PRODUCTION AND PRICE OF CELLULOSE ACETATE IN THE UNITED STATES SINCE 1920.

(Price data taken from the *Paint, Oil, and Drug Reporter;* production data estimated.)

tures, although under somewhat more mild conditions than those of Franchimont. The products obtained under these conditions were insoluble in alcohol but soluble in chloroform. Miles distinguished between fully esterified acetate and his new partially hydrolyzed product as, respectively, chloroform-soluble and acetone-soluble derivatives. More recently, lower temperatures of esterification have been employed, such as those described by Dreyfus,[19] in which the initial esterification mixture is cooled to below 0°C. and during reaction is allowed to increase in temperature to a maxi-

[18] A. Franchimont, *Compt. rend.*, 89, 711 (1879).

[19] H. Dreyfus, U. S. Patent 1,280,975 (Oct. 8, 1918).

mum of 20–30°C., giving a cellulose triacetate insoluble either in chloroform or chloroform-alcohol mixtures. Commercial processes employed today yield triacetate of this variety. Tetrachloroethane and mixtures of methylene chloride with alcohol are among the few good solvents for this product.

Numerous catalysts have been recommended for cellulose acetate manufacture, but none has offered outstanding advantages over sulfuric acid. This acid was employed by Franchimont[18] in his early work on cellulose acetylation and has since become the most standard agent for commercial use. A great many patents have been issued describing its use in acetylation procedures. The quantity of catalyst used varies widely depending upon the temperature of esterification and reactivity of the cellulose employed. Ost[20] compared sulfuric acid and zinc chloride as acetylation catalysts. Quantities of 50–100% of the weight of the cellulose and comparatively high reaction temperatures were required with zinc chloride, while sulfuric acid gave good results under mild temperature conditions with 5–10% of the weight of the cellulose. Patents covering the use of these catalysts for cellulose acetate manufacture agree in general with these data.

Perchloric acid is an exceptionally strong esterification catalyst and has been patented for use in acetylation of cellulose.[21] It has so far shown no indications of replacing sulfuric acid in commercial use, however, because of its highly corrosive action on the metal equipment now used for the preparation of cellulose esters.

Methanesulfonic acid in quantities of at least 50% of the weight of the cellulose[22] is reported to be an effective catalyst for esterification with anhydrides of acids as high as eight carbon atoms. Aromatic sulfonic acids have also been used as esterification catalysts[23] but are not as effective as sulfuric acid.

The effective strength of acidity of a catalyst is the predominate factor in its activity. The acetylation reaction being carried out in an anhydrous medium, evaluation of catalysts must be considered from the point of view of nonaqueous systems. The work of Brønsted[24] has shown that ionization

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[20] H. Ost, *Z. angew. Chem.*, **32**, 66 (1919).

[21] C. J. Malm, U. S. Patent 1,645,915 (Oct. 18, 1927); D. Krüger and F. Hohn, German Patent 519,877 (Nov. 5, 1931).

[22] Societé des Usines Chimiques Rhône, Poulenc, French Patent 705,546 (June 9, 1931).

[23] H. S. Mork, A. D. Little, and W. H. Walker, U. S. Patent 709,922 (Sept. 30, 1902); French Patent 324,862 (Dec. 27, 1902).

[24] J. N. Brønsted, *Ber.*, **61B**, 2049 (1928).

must be regarded as related to the solvent system employed. Conant and Hall[25] found that in acetic acid solution a number of amides and other materials, which in aqueous media do not form salts with acids, exhibit salt-forming behavior; these present a system of acid-base equilibria which can be titrated. Measurements of acidities of several mineral acids in glacial acetic acid agree remarkably with their behavior as acetylation catalysts. Sulfuric and perchloric acids in acetic acid solution were termed superacid solutions because of their exceptional strength as compared with other acids. Hydrochloric, phosphoric, and nitric acids in glacial acetic are comparatively weak, as are the organic sulfonic acids.

Sulfuric acid has an additional advantage over other proposed catalytic agents in that it is very highly adsorbed onto cellulose fibers from acetic acid-anhydride solution, resulting in high effective concentrations of catalyst on the surface of the fiber at the time of initial esterification.

Sulfuric acid undergoes chemical changes in the presence of acetic anhydride. Franchimont[26] reported that sulfoacetic acid was formed by action of acetic anhydride and assumed that acetylsulfuric acid was an intermediate product. Stillich[27] showed that acetylsulfuric acid is readily formed at low temperatures, and at elevated temperatures in presence of an excess of acetic anhydride quantitative conversion to sulfoacetic acid takes place. Van Peski[28] studied the reactions of acetic and sulfuric acids in detail, and isolated acetylsulfuric acid. It has been suggested that this mixed anhydride is the esterification agent of cellulose, the sulfuric acid then being regenerated to react with more anhydride. It seems probable, however, that the strongly acidic condition provided by the catalyst makes possible direct esterification by acetic anhydride as a primary reaction. During or prior to the acetylation reaction, a proportion of the sulfuric acid catalyst is combined with cellulose as the sulfate. This is brought about by direct action of sulfuric acid in glacial acetic acid, but in presence of anhydride it can also be explained by reaction of the mixed anhydride. The extent of sulfate formation increases with increased catalyst concentration. Use of quantities of sulfuric acid catalyst equal to the weight of cellulose results in an esterified product soluble in water.[29] There is evidence that in the later stages of acetylation some replacement of combined sulfuric acid by acetic acid takes place.

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[25] J. B. Conant and N. F. Hall, *J. Am. Chem. Soc.*, **49**, 3047 (1927).
[26] A. Franchimont, *Compt. rend.*, **92**, 1054 (1881).
[27] O. Stillich, *Ber.*, **38**, 1241 (1905).
[28] A. J. Van Peski, *Rec. trav. chim.*, **40**, 103 (1921).
[29] T. Araki, *J. Soc. Chem. Ind., Japan*, **43**, suppl. binding, 49 (1940).

The equations involved in an acetylation reaction would thus be:

$$\underset{\text{Cellulose}}{R_{cell}—(OH)_n} + n(CH_3CO)_2O \xrightarrow{(H_2SO_4)} \underset{\text{Cellulose acetate}}{R_{cell}(OOC\cdot CH_3)_n} + nCH_3COOH \quad (1)$$

$$\underset{\text{Cellulose}}{R_{cell}—(OH)_n} + nH_2SO_4 \longrightarrow \underset{\text{Cellulose sulfate}}{R_{cell}(SO_4H)_n} + nH_2O \quad (2)$$

$$(CH_3CO)_2O + H_2SO_4 \rightleftharpoons \underset{\text{Acetylsulfuric acid}}{CH_3CO\cdot SO_4H} + CH_3COOH \quad (3)$$

$$\underset{\text{Cellulose}}{R_{cell}—(OH)_n} + n\underset{\text{Acetylsulfuric acid}}{CH_3CO\cdot SO_4H} \longrightarrow \underset{\text{Cellulose acetate}}{R_{cell}(OOC\cdot CH_3)_n} + nH_2SO_4 \quad (4)$$

$$\underset{\text{Cellulose}}{R_{cell}—(OH)_n} + n\underset{\text{Acetylsulfuric acid}}{CH_3CO\cdot SO_4H} \longrightarrow \underset{\text{Cellulose sulfate}}{R_{cell}(SO_4H)_n} + nCH_3COOH \quad (5)$$

$$\underset{\text{Cellulose sulfate}}{R_{cell}(SO_4H)_n} + nCH_3COOH \longrightarrow \underset{\text{Cellulose acetate}}{R_{cell}(OOC\cdot CH_3)_n} + nH_2SO_4 \quad (6)$$

$$\underset{\text{Acetylsulfuric acid}}{CH_3CO\cdot SO_4H} \xrightarrow[(CH_3CO)_2O]{\Delta} \underset{\text{Sulfoacetic acid}}{HSO_3\cdot CH_2COOH} \quad (7)$$

Combined sulfate results in very poor stability of cellulose acetate and must be reduced to an insignificant quantity in the final product. In the manufacture of acetone-soluble products, this may be accomplished incidental to the acid hydrolysis, but in the case of fully esterified esters its removal must be given special consideration. Some processes employ very small amounts of catalyst which minimize the quantity of sulfate formation.

Boiling water has often been recommended as an effective stabilization treatment. Modifications designed to give improved results include use of superheated steam[30] instead of boiling water, or treatment in an autoclave to permit use of higher temperatures.[31] Boiling water acidified with either organic or mineral acids has also been recommended as a stabilization treatment.[32] In all of these treatments, the essential requirement is removal of sulfate without appreciable hydrolysis of acetyl groups. The sulfate groups are quite readily removed by boiling water if the free acid group of the sulfate is in the acid form. Should the unstable product be given an opportunity to react with sodium or potassium salts before stabilization, the action of boiling water is comparatively ineffective, since alkali metal salts of the cellulose sulfate are very resistant to hydrolysis. If left in the final product, the sulfuric acid leads to instability toward heat even if partially neutralized with alkali metals.

Salts of alkaline earth or heavier metals may be used to neutralize the

[30] C. Dreyfus and H. Martin, U. S. Patent 2,071,333 (Feb. 23, 1937).

[31] Wolff and Co., German Patents 440,844 (Feb. 12, 1927); 511,020 (July 10, 1930).

[32] I. G. Farbenindustrie Akt.-Ges., Brit. Patent 299,326 (Mar. 24, 1930).

acidity of the combined sulfate and give stable products. Magnesium salts have been recommended, as have those of calcium, barium, and aluminum. These may be used in just sufficient quantity to neutralize the sulfate, or may be added in excess and allowed to remain on the product. Such treatments result in increased ash content of the product, but may be beneficial if maintained low enough in quantity so as not to produce hazy solutions.

Solution Process. In discussing the manufacture of cellulose acetate, the description will be confined to a method employing sulfuric acid as a catalyst. The following operations are usually involved:

Pretreatment. Cellulose such as purified cotton linters or wood pulp will absorb, under normal conditions, from 5 to 10% moisture from the air, and it is desirable before acetylation to reduce this value. Excessive temperatures in the drying operation often cause poor penetration of reagents during esterification, especially if the cellulose has received strong chemical treatment such as alkaline bleaches, or treatment with strong alkali during purification. It is also important that the moisture content of the cellulose be not reduced to too low a figure. Completely dried cellulose, even if dried under mild temperature conditions, is difficult to esterify uniformly, giving rise to residual unreacted fiber and poor uniformity of product.

Acetylation of cellulose is a heterogenous reaction, the cellulose being suspended in the reaction medium and passing gradually into solution after esterification has taken place. The course of the reaction has been found by Sakurada[33] to be largely controlled by diffusion rates into the cellulose fiber. Hess and Trogus[34] have observed changes in x-ray diagrams from that of cellulose to that of the reaction product after the initial surface reaction of esterification, after which the reaction depends upon diffusion into the inner part of the fiber. The physical condition of the cellulosic material is thus of primary importance to the quality of the product. Only under conditions of uniform reaction can products free from insoluble particles, unesterified fiber, and hazy appearance in solution be obtained. The result has been application of a pretreatment step in cellulose acetate manufacture, with the object of rendering the entire mass of cellulose as uniformly reactive as possible.

Of the many modifications which have been recommended for pretreatment, the most common is treatment with acetic acid either alone or in the presence of part or all of the esterification catalyst. In an early patent,

[33] I. Sakurada, *J. Soc. Chem. Ind., Japan*, **35**, suppl. binding, 3, 283 (1932).

[34] K. Hess and C. Trogus. *Z. physik. Chem.*, **B15**, 157 (1931).

Wohl[35] described steeping cellulose in acetic acid and then pressing out the excess liquid before acetylation. Hot acetic acid[36] or its vapors[37] have also been patented as pretreatment agents. Use of catalysts in the pretreatment step is included in many process modifications. Aqueous acetic acid is more effective than glacial in producing a reactive cellulose,[38] but, inasmuch as any water remaining from pretreatment must later be destroyed by additional anhydride, glacial acid is usually used. The quantity of pretreatment acid may vary widely, according to the convenience of the process employed.

While the temperature of pretreatment may range from 20°C. to the boiling point of acetic acid or above, it is usually maintained below 50°C. to avoid losses through evaporation. In absence of catalyst, this treatment causes only slight reduction of viscosity of the cellulose. In presence of catalyst, the cellulose viscosity drops rapidly. Cellulose employed for acetylation has usually many times the viscosity it is to possess after acetylation, and at some step in the process the viscosity will be greatly reduced. Werner[39] has studied the reduction of viscosity during esterification. This action is brought about by the catalyst, and will occur, therefore, mainly in the pretreatment step if catalyst is present, and, if it is not, will take place simultaneously with acetylation.

Acetylation. The acetylation of cellulose should be allowed to proceed sufficiently slowly so that the reaction temperature can be controlled, and, since the reaction is accompanied by evolution of a considerable quantity of heat, the esterifying anhydride must be added at a comparatively low temperature. This will vary in different processes, the degree of cooling required being in general dependent upon the amount of catalyst used and the desired viscosity of the final product.

An amount of acetic anhydride, somewhat in excess of that necessary to esterify the cellulose and to take care of any moisture present at the end of the pretreatment, is added after the cooling operation has brought the temperature to the proper point, and, if the catalyst has not been previously added to aid in pretreatment, it must also be introduced at this time.

During the early stages of acetylation, the reaction should be well controlled by external cooling to prevent too rapid a temperature rise. As the

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[35] A. Wohl, Brit. Patent 20,527 (July 17, 1913); French Patent 448,072 (Jan. 22, 1913).

[36] H. T. Clarke and C. J. Malm, U. S. Patents 1,668,944–5 (May 8, 1928).

[37] H. Dreyfus, Brit. Patent 263,939 (Jan. 6, 1927).

[38] H. Dreyfus, Brit. Patent 343,986 (Feb. 16, 1931).

[39] K Werner, *Cellulosechem.*, **12**, 320 (1931).

reaction proceeds, it may be allowed to increase gradually in temperature to a maximum which should be well controlled to insure proper viscosity of product. Proper correlation of the initial speed of reaction, maximum temperature, and total time of esterification is important in production control and must be maintained in balance.

Complete solution of the cellulose indicates the end of the esterification reaction, and the temperature is then held constant until the solution viscosity, which drops slowly under these conditions, is found by control test to be at the proper point. Care must be taken not to allow the reaction to continue for too long a time after acetylation is completed if small catalyst concentrations are employed, since gelling will take place.

Hydrolysis. The acetylation reaction is stopped by the addition of sufficient water to destroy any acetic anhydride remaining in the reaction mixture and to bring the water content of the solution usually to 5–10%. This is best added in the form of aqueous acetic acid to prevent precipitation of the cellulose acetate. During the addition of this solution, beyond the point where anhydride is being decomposed, there is considerable removal of combined sulfate. This is especially effective if the temperature is above 40°C.

Further quantities of sulfuric acid may be added with the aqueous acetic solution, if this is desirable to speed up the hydrolysis step which is to follow. Neutralizing agent may be added if large amounts of sulfuric acid were employed in the esterification.

The reaction solution as obtained after addition of the aqueous acetic acid is now ready to undergo an acid hydrolysis to remove some of the acetyl groups. In order that this be a uniform reaction, it is necessary to maintain uniform temperature until the desired degree of hydrolysis has been obtained. This temperature may be chosen to suit the equipment and convenience of the process, the rate of reaction for a given concentration of catalyst being, of course, faster, the higher the temperature. It is usually carried out somewhat above room temperature to avoid refrigeration, and should not be maintained too high because of the danger of degradation of the cellulose.

The higher the ratio of water to sulfuric acid in the hydrolysis solution, the less will be the degradation at a given temperature. The susceptibility of the acetate to degradation increases with decrease in acetyl content, and, if it is desirable to carry out a rapid hydrolysis with large quantities of sulfuric acid, water should be added during the process.[40] Hydrolysis under

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[40] C. J. Malm and C. L. Fletcher, U. S. Patent 2,013,830 (Sept. 10, 1935).

ordinary conditions may be carried to as low as 30% acetyl. At about this point the usual reaction solutions containing on the order of 10% water become poor solvents for the acetate, and gelatinous precipitation begins to take place. By addition of larger quantities of water to reduce the acetic acid strength to 60 or 70%, the hydrolysis may be continued to acetyl values below 20%, at which point the product becomes completely water-soluble and must be isolated by precipitation into organic solvents such as acetone or alcohol.[41] Continued hydrolysis below about 13% acetyl results in regeneration of essentially deacetylated cellulose which is insoluble in water and organic solvents.

During the course of the hydrolysis, test samples may be taken, by which the time of hydrolysis to give any desired acetyl value may be determined.

Purification. At the time when control tests have indicated that the proper degree of hydrolysis has been reached, the cellulose acetate is precipitated from solution, usually by pouring the reaction solution with good agitation into a large volume of water.

The most important objects in this operation are to produce a precipitated material which is readily penetrated by water so that it may be easily washed to remove all uncombined acids, and to obtain, for recovery, acetic acid of as high concentration as possible. A stream of viscous solution poured into the water will usually result in formation of "skins" of precipitated material containing entrapped solution into which it is difficult for water to penetrate. For this reason, if solutions are precipitated directly into water, they must be first diluted to a low viscosity. A more practical procedure for commercial use is to precipitate the solution into dilute acetic acid, keeping the concentration of the precipitation acid within a range of 25 to 35% acetic acid by simultaneous addition of reaction solution and dilute acid.[42]

The process of washing must be given careful consideration in commercial operation because it is necessary to recover the acetic acid. The cost of recovery increases rapidly with increased dilution. The original precipitation liquor is first drained off, and means are then employed to remove as much as possible of the acid still withheld by the cellulose acetate by as small an amount of water as possible. After this has been accomplished, the product is thoroughly washed with water to remove last traces of acetic acid and catalyst.

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[41] C. R. Fordyce, U. S. Patent 2,129,052 (Sept. 6, 1938).

[42] H. T. Clarke, U. S. Patent 1,823,348 (Sept. 15, 1931); French Patent 693,133 (Nov. 17, 1930); Brit. Patent 342,596 (Feb. 5, 1931).

The quality of water employed for washing is important to the quality of the product. Good clarity and color can be obtained only by use of a good clear wash water free from iron and other color-causing substances.

The final operation in cellulose acetate manufacture is drying. The last wash water is removed and the product dried to a low moisture content. It is desirable to remove as much water as possible by a centrifuge, press, or similar equipment.

The recovery of used acetic acid, mentioned above as an essential step in cellulose acetate manufacture from an economic point of view, is rendered difficult by the fact that vapor-pressure relationships prevent easy separation of water and acid by fractional distillation. Early recovery methods involved evaporation to obtain sodium acetate. Present processes, however, use extraction or azeotropic distillation.

A great many acetylation methods in use or covered by patents may be fitted into the operations described above. Comprehensive reviews of these processes have been compiled by Faust,[43] Worden,[44] and Krüger.[45] The following procedure will serve as an example of an acetylation process employing these steps:

After suitable drying, 100 parts of cotton linters are added to 700 parts of glacial acetic acid in a sigma-blade acetylation mixer, and soaked for 4 hrs. at 100°F. The mass is then cooled to 70°F. and to it is added a mixture, previously prepared and cooled to 0°F., of 310 parts of 85% acetic anhydride and 7.2 parts of sulfuric acid. The initial reaction is kept from going to too high a temperature by means of water at 40°F. circulated through the mixer jacket. After a short time, the reaction temperature is permitted to rise gradually to a maximum of 70–80°F. and is held there until a uniform solution of desired viscosity is obtained. Then 220 parts of 50% acetic acid is added, and the temperature of the solution is allowed to rise to above 100°F. during its addition. The temperature is then adjusted to 100°F. and held constant until the desired degree of hydrolysis is attained. The cellulose acetate is then precipitated, stabilized, thoroughly washed, and dried.

Modified Solution Processes. Numerous variations of procedure for the manufacture of cellulose acetate have appeared in the patent literature. A great many of these are concerned with details of processes essentially as described above. A few involve major changes and are worthy of note.

The use of zinc chloride as catalyst has been employed on a production scale. Its advantages lie in better solubility of the triacetate in an acetic

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[43] O. Faust, *Celluloseverbindungen*. J. Springer, Berlin, 1935.

[44] E. C. Worden, *Technology of Cellulose Esters*. Vol. VIII, Van Nostrand, New York, 1915.

[45] D. Krüger, *Zelluloseazetate*. T. Steinkopff, Dresden and Leipzig, 1933.

acid-zinc chloride mixture, which prevents gelling, and in good stability of the resulting product. The presence of zinc chloride in the precipitation liquor, however, complicates the recovery of acetic acid.

Several solvents other than acetic acid have been recommended for acetylation media, but of these only the chlorinated hydrocarbons[46] and sulfur dioxide are of interest. Of the chlorinated solvents, methylene chloride is being used on production scale. Its excellent solvent power for cellulose triacetate makes it possible to obtain products of very high viscosity using low catalyst concentration, which in an acetic acid reaction bath would result in gelling. The small amount of catalyst is advantageous in giving only minor quantities of combined sulfate in the product. Because of the low boiling point of methylene chloride, its use has been suggested to control the acetylation reaction temperature by evaporation.[47]

Sulfur dioxide is a good solvent for cellulose acetate and has been employed as a reaction solvent in a process which has been tried out on a commercial scale.[48] A closed reaction vessel is used. After loading the cellulose, a solution of acetic anhydride, liquid sulfur dioxide, and sulfuric acid catalyst is introduced under suitable pressure. The reaction temperature is conveniently controlled by pressure variation to permit necessary evaporation of sulfur dioxide, which is returned to the reaction chamber by reflux condensation and absorbs excessive heat of reaction.

Hydrolysis to acetone solubility[49] may be carried out in the customary way by adding enough water to destroy excess acetic anhydride and to supply 3 to 10% water to the reaction mixture, and, if desired, by supplying additional sulfuric acid to increase the speed of hydrolysis.

Fibrous Acetylation Processes. If sufficient quantities of a liquid component which is not a solvent for cellulose acetate are included in an acetylation bath, the reaction product may be prevented from dissolving, resulting in a fibrous esterification. Such reactions proceed in much the same manner as in the solution methods. Similar temperatures and catalyst concentrations are used, but usually somewhat larger proportions of liquid to cellulose are necessary because of the bulk of the fibrous material as compared with equal amounts in viscous solution.

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[46] R. Hofmann, U. S. Patent 2,126,190 (Aug. 9, 1938); Brit. Patent 337,366 (Oct. 27, 1930); French Patent 697,156 (Jan. 13, 1931); German Patent 526,479 (June 6, 1931); H. LeB. Gray, U. S. Patent 1,823,359 (Sept. 15, 1931).

[47] L. E. Clement, U. S. Patent 2,104,023 (Jan. 4, 1938).

[48] L. M. Burghart, U. S. Patent 1,816,564 (July 28, 1931).

[49] L. M. Burghart, U. S. Patent 1,822,563 (Sept. 8, 1931).

In an early process of this type, Lederer[50] employed carbon tetrachloride as the inert component. Aromatic hydrocarbons are the liquids most commonly recommended for use, although other inert diluents such as ethers and aliphatic hydrocarbons which do not react with acetic anhydride or interfere with the action of the catalyst may be employed. The value of a nonsolvent depends largely upon its ability to maintain the cellulose in a swollen and easily penetrable condition throughout the esterification, while at the same time preventing dissolution. Thus, when aliphatic hydrocarbons are used, an auxiliary solvent such as methylene chloride, ethylene chloride, or sulfur dioxide improves the speed of the reaction and uniformity of the resulting product.

A serious disadvantage to the fibrous esterification process is that only fully esterified products can be made by its use. Hydrolysis to acetone-soluble material must be carried out in solution to give uniform products. No method of hydrolysis in suspension has yet proved sufficiently successful to achieve commercial use. Fibrous products which are somewhat less than fully esterified may be prepared by processes of Sindl[51] in which large quantities of sulfuric acid catalyst are employed under conditions which encourage high cellulose sulfate formation. The product is then treated with esters such as ethyl acetate at elevated temperatures to remove the sulfate, leaving unesterified hydroxyl groups.

The following esterification procedure[52] serves as an example of the fibrous acetylation process:

> Cellulose (100 parts) is submerged in glacial acetic acid. After digestion for 4 hrs. most of the liquid is removed by centrifuging, whereupon the cellulose thus treated is introduced into an acetylating mixture, which has been cooled to about 5°C. and consists of 315 parts by weight of 90–91% acetic anhydride, 363 parts acetic acid, 705 parts toluene, and 1 part of 70% perchloric acid. The acetylating reaction is carried through at a temperature slowly increasing up to 20–25°C. When samples of the fibers are shown to be soluble in a mixture of 9 parts chloroform and 1 part ethyl alcohol, all the fibers are separated from the acetylation mixture by centrifuging, whereupon they are carefully washed with water and dried. They now show a rather woolly appearance and consist substantially of cellulose triacetate.

(*c*) *Cellulose Propionate*

Cellulose propionate may be prepared by esterification with propionic anhydride in the presence of acid catalysts[53] under conditions similar to

[50] L. Lederer, U. S. Patent 999,236 (Aug. 1, 1911); Brit. Patent 3103 (Feb. 7, 1907); French Patent 374,370 (Feb. 7, 1907); German Patent 200,916 (July 31, 1908).

[51] O. Sindl and G. Frank, U. S. Patent 2,143,332 (Jan. 10, 1939).

[52] R. Müller, M. Schenck, and W. Wirbatz, U. S. Patent 2,045,161 (June 23, 1936).

[53] C. Dreyfus and G. Schneider, U. S. Patent 1,824,877 (Sept. 29, 1931).

those used for cellulose acetate manufacture. The anhydride is somewhat less reactive, however, than acetic anhydride, requiring special consideration for the conditions of pretreatment and catalyst concentration.

Mild hydrolysis of cellulose tripropionate results in a product soluble in benzene and in butyl acetate. Further hydrolysis of cellulose propionate is reported by Fothergill[54] to give products of particular interest. The hydrolysis is carried out so as to give a product of about 64% combined propionic acid which is insoluble in benzene but soluble in butyl acetate and acetone. Still further hydrolysis results in products insoluble in both benzene and butyl acetate but soluble in acetone, methyl Cellosolve, and dioxane. A particularly good solvent combination for making films and plastics from this cellulose propionate is claimed to be a mixture of 62 parts of acetone, 21 parts of butyl acetate or other nonsolvent component to act as a residual swelling agent, and 17 parts of alcohol.

Cellulose tripropionate is considerably softer than either the triacetate or its hydrolysis product. Up to the present time it has not been prepared in commercial quantities.

(*d*) *Cellulose Butyrate*

Cellulose butyrate, similar to the propionate, may be prepared by esterification with the anhydride and a catalyst such as sulfuric acid, provided the reaction conditions are adjusted to permit an efficient pretreatment and well-controlled esterification. Esselen and Mork[55] in 1922 recommended the use of small quantities of water with butyric acid as a pretreatment step.

Hydrolysis of cellulose tributyrate has been described by Gault and Angla[56] who carried out the reaction in butyric acid of 76–78% strength at a temperature of 45–50°C. Increased hydrolysis results in changes of solubility, the least hydrolyzed materials being soluble in benzene but insoluble in methyl alcohol, further reaction yielding products soluble in both benzene and methyl alcohol, and, finally, products soluble in alcohol but insoluble in benzene.

Herzog and Frank[57] have described a process for the preparation of hy-

[54] R. E. Fothergill, U. S. Patent 2,076,555 (Apr. 13, 1937); Brit. Patent 449,182 (June 22, 1936).

[55] G. J. Esselen and H. S. Mork, U. S. Patent 1,425,580 (Aug. 15, 1922).

[56] H. Gault and B. Angla, U. S. Patent 1,912,189 (May 30, 1933); French Patent 685,637 (July 12, 1930).

[57] R. O. Herzog and G. Frank, French Patent 700,165 (Aug. 7, 1930); G. Frank and H. Cohn, *Cellulosechem.*, **12**, 68 (1931).

drolyzed cellulose butyrates involving preliminary treatment of cellulose with 87% formic acid at 20°C. This product, which contains a small amount of combined formic acid, is then washed and dried and thereafter esterified with a butyric anhydride and butyric acid mixture using zinc chloride as a catalyst. The reaction product is isolated and then hydrolyzed in 95% butyric acid at 90°C. for 32 hrs. It is soluble in acetone and in mixtures of benzene and alcohol.

Cellulose tributyrate melts at a lower temperature than either the acetate or propionate and is considerably softer than those esters. The product has not been made in commercial quantities up to the present time.

(*e*) *Mixed Esters of Lower Aliphatic Acids*

Cellulose mixed esters containing, in addition to acetyl, either propionyl or butyryl groups offer the opportunity of obtaining products with certain physical properties improved over cellulose acetate, at the same time being free from the disadvantages of softness, low strength, and the difficulty of manufacture of cellulose propionate and butyrate.

These mixed esters are commercially manufactured by including the acyl components in the esterification bath in the form of acids or anhydrides. Clarke and Malm[58] have pointed out that acyl groups from propionic or butyric acid may be introduced into a cellulose ester without employing the anhydride, if these acids are present in an esterification mixture in which some other active anhydride is present. Propionic acid may in this way be incorporated with acetic anhydride or a mixture of acetic anhydride and acetic acid to produce a uniform product of good quality containing both acyl groups. It is also possible to esterify with propionic or butyric anhydrides with acetic acid present in the reaction mixture to produce a mixed ester. The ratio of acetic and propionic or butyric acids obtained in the cellulose derivative will be proportional to the concentration of the corresponding acyl groups in the esterification mixture, making possible accurate control in manufacture. Pretreatment is an important step in the preparation of cellulose mixed esters of satisfactory quality and should be so adjusted as to insure uniform esterification and freedom from haze and undissolved fiber in the reaction product.

A procedure for preparation of cellulose acetate propionates of high viscosity has been described by Malm.[59] In a process for manufacturing

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[58] H. T. Clarke and C. J. Malm, U. S. Patent 2,048,685 (July 28, 1936).

[59] C. J. Malm, U. S. Patent 2,026,986 (Jan. 7, 1936).

nixed esters containing moderate amounts of butyryl, Billing and Tinsley[60] nave recommended pretreatment with acetic acid followed by esterification vith butyric acid and acetic anhydride using a suitable catalyst.

Mixed esters containing very high proportions of propionyl or butyryl groups require especially designed procedures for their manufacture. Gardner[61] has described a method using from 5–20% water, based upon the weight of the cellulose, in pretreatment mixtures in which acids of three to four carbon atoms predominate. The presence of this amount of moisture is very effective in bringing about a uniform esterification reaction.

The hydrolysis of fully esterified mixed esters containing at least 15% propionyl or butyryl groups has been reported by Malm and Fletcher[62] to bring about changes in solubility and physical properties which make the products more desirable than the unhydrolyzed esters.

(*f*) *Higher Aliphatic Acid Esters*

Anhydrides of organic acids containing more than four carbon atoms cannot readily be made to esterify cellulose by use of acid catalysts, and these esters therefore require other methods of preparation. Earlier work on cellulose higher esters employed acid chlorides as esterifying agents. Grün and Wittka[63] treated cellulose with lauryl and stearyl chlorides in pyridine at "the temperature of a water bath," and obtained partially esterified products which were not changed in appearance from the original cellulose.

Karrer,[64] using cuprammonium cellulose with palmityl and stearyl chlorides and quinoline at a reaction temperature of 120°C., obtained products soluble in chloroform.

Gault and Ehrmann[65] described the preparation of several cellulose higher esters using benzene as a diluent for the pyridine and acid chloride reaction. Mono-, di-, and tri-esters of lauric, palmitic, and stearic acids were made. Products from untreated cellulose were found to be insoluble, while modified cellulose such as that regenerated from viscose or cuprammonium solution gave soluble esters. The use of benzene or toluene as a diluent for the pyridine-acid chloride reaction mixture offers a considerable improvement in operation, the hydrocarbon acting at elevated tempera-

[60] W. M. Billing and J. S. Tinsley, U. S. Patent 1,973,693 (Sept. 18, 1934).
[61] H. S. Gardner, Jr., U. S. Patent 2,113,301 (Apr. 5, 1938).
[62] C. J. Malm and C. L. Fletcher, U. S. Patent 2,026,583 (Jan. 7, 1936).
[63] A. Grün and F. Wittka, *Z. angew. Chem.*, **34**, 645 (1921).
[64] P. Karrer, J. Peyer, and Z. Zega, *Helv. Chim. Acta*, **5**, 853 (1922).
[65] H. Gault and P. Ehrmann, *Compt. rend.*, **177**, 124 (1923); *Chimie et industrie*, Special No. **574** (May, 1924); *Bull. soc. chim.*, [4], **39**, 873 (1926).

tures as a solvent for the intermediate product between the acid chloride and tertiary base. A still better diluent for this purpose is chlorobenzene, which has been used by Hagedorn.[66] Cellulose lauric acid esters made in this way from native cellulose were found to be insoluble, but were converted to soluble products by heating in suitable solvents at 135–145°C.

Kita and his coworkers[67] have shown that alkali cellulose can be made to react with acid chlorides of higher aliphatic acids to give partially esterified derivatives. The amount of acyl introduced was found to vary with the concentration of alkali present and to be independent of reaction temperatures.

Sakurada and Nakashima,[68] by repeated treatment with alkali and stearyl chloride, obtained a degree of esterification corresponding to 2.1 moles for each glucose unit.

Based upon the fact that chloroacetic anhydride does not react with cellulose to produce chloroacetyl derivatives, Clarke and Malm[3] employed this compound as an impelling agent to bring about esterification with other acids present in an esterifying mixture. Cellulose, such as cotton linter may be treated with chloroacetic anhydride and chloroacetic acid containing a catalyst, such as magnesium perchlorate, and an organic acid in sufficient quantity to esterify the cellulose. When held at a temperature above the melting point of the reaction mixture for 4 to 6 hrs., a uniform solution of the cellulose derivative results. Aliphatic acids from valeric to myristic acids react very readily when this procedure is used, while palmitic and stearic acids require a reactive form of cellulose for satisfactory results (Table 1).

Pringsheim, Lorand, and Ward[69] have reviewed various methods for the preparation of cellulose higher esters and have tested processes for conversion of insoluble derivatives to soluble products. Conditions of treatment were found to be important for the conversion, short periods of heating at temperatures of 190–200°C. being preferable to longer times at lower temperatures because of the more favorable effect on viscosity and strength of the products.

The rapidly increasing length of acyl groups which one obtains by

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[66] M. Hagedorn and O. Reichert, U. S. Patent 1,832,381 (Nov. 17, 1931); M. Hagedorn and G. Hingst, U. S. Patent 1,940,589 (Dec. 19, 1933).

[67] G. Kita, I. Sakurada, and T. Nakashima, *Cellulose Ind.* (Tokyo), **2**, 30 (1926); J. Leibowitz, *Cellulosechem.*, **9**, 125 (1928).

[68] I. Sakurada and T. Nakashima, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **6**, 197 (1927).

[69] H. Pringsheim, E. J. Lorand, and K. Ward, Jr. *Cellulosechem.*, **13**, 119 (1932).

TABLE 1

PREPARATION OF CELLULOSE ESTERS USING CHLOROACETIC ANHYDRIDE (CLARKE AND MALM[3])

Acid	Parts of acid by weight	Parts of cotton by weight	Parts of chloroacetic anhydride by weight	Parts of magnesium perchlorate by weight	Time of reaction, hrs.	Solubilities of final products at room temperature					
						In acetone	In carbon tetrachloride	In chloroform	In ether	In benzene	In ligroin
Acetic	25	5	30	0.05	3	−	−	+	−	−	−
Propionic	25	5	30	0.05	3	+	−	+	−	+	−
n-Butyric	10	3	20	0.05	4	+	+	+	−	+	−
Isobutyric	15	3	25	0.05	4	+	+	+	+	+	−
n-Valeric	15	3	25	0.05	4	+	+	+	+	+	(*a*)
Isovaleric	15	3	25	0.05	4	+	+	+	+	+	+
n-Caproic	20	5	60	0.05	4	+	+	+	+	+	+
n-Heptylic	18	4	55	0.05	8	+	+	+	+	+	+
Caprylic	25	5	60	0.05	5	+	+	+	+	+	+
Pelargonic	25	5	60	0.05	5	−	+	+	+	+	+
Capric	25	5	60	0.05	5	−	+	+	+	+	+
Lauric	20	3	20	0.05	4	−	+	+	+	+	+
Myristic	25	4	60	0.05	4	−	+	+	−	+	+
Palmitic	15	2	60	0.05	24	−	+	+	−	+	+
Stearic (com.)	15	2	60	0.05	24	−	+	+	−	+	+
Crotonic	15	5	30	0.05	5	+	−	+	−	+	−
Cyclohexane-carboxylic	10	2	15	0.02	3	−	−	+	−	−	−
Benzoic	15	3	20	0.05	8	−	−	+	−	−	−
o-Methoxybenzoic	10	2	15	0.02	4	−	−	+	−	−	−
o-Chlorobenzoic	10	2	15	0.02	5	−	−	+	−	−	−
Acetylsalicylic	20	2	20	0.05	10	−	−	+	−	−	−
Phenylacetic	15	3	20	0.05	7	−	−	+	−	−	−
Hydrocinnamic	15	3	30	0.05	3	+	+	+	−	+	−
Cinnamic	15	3	40	0.05	5	−	−	+	−	−	−
Stearic (com.) + Acetic	30 + 6	4	50	0.05	7	+	..	+	..	−	..
o-Methoxybenzoic + Acetic	10 + 2	2	15	0.02	7	+	..	+	..	−	..
Acetic	15	2	20	0.02†	3	−	..	+	..	−	..
Acetic	10	2	20	0.05*	6	−	..	+	..	−	..

Key: + soluble; − insoluble.

† Trichloroacetic anhydride was used in place of the monochloroacetic.

* β-Bromopropionic anhydride was used in place of the monochloroacetic

(*a*) Soluble in warm ligroin, insoluble at room temperature.

gressing to higher cellulose esters results in rapid loss of many of the most desirable properties of these products from the standpoint of plastics, films, textile materials, etc.

Hagedorn and Möller[70] have measured tensile strengths of several aliphatic cellulose esters and report a very rapid drop in this property with increasing size of acyl groups. Esters of acids of six to nine carbon atoms show extremely wide ranges of solubility, both in polar and nonpolar solvents, while esters of still higher aliphatic acids become less soluble in such solvents as acetone, retaining their solubility in hydrocarbons

TABLE 2

SOLUBILITIES OF CELLULOSE HIGHER TRIESTERS (FORDYCE, SALO, AND CLARKE[71])

Cellulose triester	Tetrachloroethane	Ethylene dichloride	Acetone	Ethyl acetate	Butyl acetate	Benzene	Toluene
Acetate	+	−	−	−	−	−	−
Propionate	+	+	+	+	+	+	−
Butyrate	+	+	+	+	+	+	−
Valerate	+	+	+	+	+	+	+
Caproate	+	+	+	+	+	+	+
Heptoate	+	+	−	+	+	+	+
Caprylate	+	+	−	+	+	+	+
Pelargonate	+	+	−	+	+	+	+
Caprate	+	+	−	+	+	+	+
Laurate	+	+	−	+	+	+	+
Myristate	+	+	−	−	−	+	+
Palmitate	+	−	−	−	−	+	+
Stearate	+	−	−	−	−	+	+

Key: + soluble; − insoluble.

(Table 2). Melting points of the higher cellulose esters drop very rapidly from cellulose acetate to the valerate, above which the melting points remain low. In quantitative evaluation of data covering such a series of cellulose derivatives, however, it should be kept in mind that esters of high-molecular-weight acids require drastic chemical treatment in their preparation, which results in quite severe degradation of the cellulose. Variations in the amount of degradation may readily account for quite wide discrepancies in reported data.

Cellulose mixed higher esters, particularly those containing a substantial amount of acetyl and a higher-molecular-weight acid, have very interesting

[70] M. Hagedorn and P. Möller, *Cellulosechem.*, **12**, 29 (1931).

[71] C. R. Fordyce, M. Salo, and G. R. Clarke, *Ind. Eng. Chem.*, **28**, 1310 (1936).

properties. These mixed esters may be readily prepared from acetone-soluble cellulose acetate by esterification of the free hydroxyl groups with the desired high-molecular-weight acid. This may be accomplished either by heating a pyridine solution of the cellulose acetate with a large excess of the higher acid chloride[72] or by the use of chloroacetic anhydride and the higher acid. The resulting product shows a wide range of solubility in ketones, esters, and mixtures of toluene with alcohol. It is highly compatible with a large variety of resins, fats, and oils. The product is very highly resistant to sorption of moisture.

Cellulose esters of naphthenic acids have been prepared by Kita, Mayume, Sakrada, and Nakashima[73] by a variety of reaction processes. Anhydrides gave only low degrees of esterification; acid chlorides yielded products between the di- and tri-esters. Complete esterification was not obtained. Patents have described reaction of naphthenic acid chlorides upon cellulose in the presence of picoline and chlorobenzene at a temperature of 135°C.[74] Mixed esters have also been prepared by esterification of cellulose with mixtures of aliphatic and naphthenic acid chlorides on alkali cellulose[75] or in the presence of a tertiary base.[76]

(g) *Uses of Aliphatic Fatty Acid Esters*

Cellulose acetate and mixed esters of acetic and either propionic or butyric acids are now manufactured in large commercial quantities. Cellulose triacetate, while the first of these derivatives to be made, has never become commercially popular because of its limited solubility. Recently, in an effort to take advantage of the higher melting point and improved moisture resistance of this material over acetone-soluble acetate, there has been some tendency to return to the highly esterified product. Methylene chloride, which is now more readily available than in previous years, has contributed to the trend, since this solvent in mixtures with alcohol forms good solutions of triacetate. Even with this possibility, however, no appreciable use of triacetate has resulted so far

The acetone-soluble cellulose acetates include products ranging from 36–42% acetyl content and have been most widely used materials. Acetone has been the standard solvent for most uses, but several other readily

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[72] H. Gault and P. Ehrmann, *Caoutchouc & gutta-percha*, **24**, 13748, 13824 (1927).
[73] G. Kita, T. Mayume, J. Sakrada, and T. Nakashima, *Kunststoffe*, **16**, 167 (1926).
[74] I. G. Farbenindustrie Akt.-Ges., Brit. Patent 305,947 (June 11, 1930).
[75] M. Hagedorn, U. S. Pateht 1,994,608 (Mar. 19, 1935).
[76] M. Hagedorn and P. Möller, U. S. Patent 1,975,897 (Oct. 9, 1934).

available compounds such as methyl acetate, ethyl lactate, diacetone alcohol, ethylene glycol monomethyl ether, dioxane, and mixtures of ethylene chloride with alcohols, are also widely used, as well as appreciable quantities of diluents such as ethyl acetate, ethyl methyl ketone, and methyl, ethyl, and butyl alcohols.

Cellulose acetate rayon, manufactured by dry spinning from acetone solution, has been largely responsible for the great growth of acetate manufacture. Concentrated acetone solutions are forced through spinnerets to form filaments, which are cured by circulated air, then gathered and passed over guide rolls to apply controlled twisting and stretching. The earliest descriptions of dry spinning of cellulose acetate were given in patents of Bayer and Co.,[77] although before that time wet spinning processes, involving spinning of acetic acid or chloroform solutions into precipitating liquids, were described by Wagner[78] and by Little, Walker, and Mork.[78] The first large-scale manufacture of cellulose acetate rayon in the United States was in 1926. Rapid expansion continued from that time, resulting in an increase of from 2,620,000 pounds of acetate rayon manufactured in 1926 to nearly ten million pounds in 1930. Rayon uses increased another fivefold in the next five years, and again threefold between 1935 and 1940; present annual acetate production in this country for rayon use is estimated to be at least 180,000,000 pounds.

Acetate photographic film base has replaced the hazardous cellulose nitrate for x-ray, portrait, amateur Ciné, and several other types of films, and the uses of cellulose acetate sheet stock of varying thickness for miscellaneous purposes, such as packaging containers, is appreciable. Most cellulose acetate film, including that for photographic purposes, is manufactured from viscous solutions in volatile organic solvents, such as acetone, by flowing the solution in proper thickness onto a moving polished surface, and, after evaporation of solvent, continuously removing the film. Other films, particularly those of greater thickness, are made by extrusion of heavy pastes containing a minimum quantity of volatile solvent through a suitable orifice. In the latter products, appreciable quantities of plasticizers which are good solvents for the acetate at elevated temperatures are included, and assist in the extrusion operation, while films for uses in which strength or rigidity are important are made by the former process

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[77] Bayer and Co., Brit. Patent 28,733 (Nov. 2, 1905); French Patent 350,422 (Jan. 4, 1906).

[78] A. Wagner, German Patents 137,255 (June 5, 1901); 152,432 (May 4, 1901); A. D. Little, W. H. Walker, and H. S. Mork, U. S. Patents 712,000 (Oct. 28, 1902); 792,149 (June 13, 1905).

and contain lower quantities of plasticizers which may or may not be active solvents for the acetate even when hot.

In the field of plastics, cellulose acetate molding compositions have become important within the last decade. Earlier processes for preparing molding compounds, in which the acetate, plasticizer, and pigment, etc., were mixed in solution, blocked, and skived, were during this time replaced by more rapid compounding methods, such as working the plastic compositions on heated rolls without use of solvent.[79] Slow molding methods of the compression type, which were time-consuming for heating and cooling cycles, were also replaced by injection molding which made possible rapid operation and the molding of several pieces at a time.

For successful molding compositions, plasticizers permitting suitable flow at high temperatures together with satisfactory physical characteristics in the final product are a vital factor.

Only minor quantities of cellulose acetate have been used in lacquers, mainly because of the limited solubility of the cellulose ester in suitable solvents and its incompatibility with most resins in quantities necessary to produce good adhesion and surface hardness.

Mixed cellulose esters have been most useful in supplying material for products in which cellulose acetate has been found to some degree unsatisfactory. Mixed esters have, in general, wider solubilities than do acetates of the same degree of substitution. Then, too, mixed esters containing appreciable quantities of the higher acids have been shown to have reasonably good compatibility with lacquer resins.[71]

The physical properties of the mixed esters of cellulose have been thoroughly studied, and the results have been published recently.[80] These properties are best shown on triangular diagrams where the composition of any mixed ester from pure acetate to pure propionate or butyrate may be represented. Melting points vary from a value of 300°C. for high-acetyl cellulose acetate to 200°C. for cellulose acetate propionates of high propionyl content and for cellulose propionates, and to 160°C. for cellulose acetate butyrates of high butyryl content and for cellulose butyrates. Sorption of moisture at different relative humidities varies widely and is greatly diminished with increased higher acyl content.

Considering that both cellulose acetate and mixed esters are now available on the market, the physical properties of any one compound may be expected to determine which is to be used in a particular application. For

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[79] F. R. Conklin, U. S. Patents 2,048,686 (July 28, 1936); 2,155,303 (Apr. 18, 1939).
[80] C J. Malm, C. R. Fordyce, and H. A. Tanner, *Ind. Eng. Chem.*, **34**, 430 (1942).

photographic films, where moisture resistance and tensile strength are important factors, advantages are to be gained by the use of mixed esters containing sufficient quantities of higher acids to prevent undesirable curl with changes in humidity, at the same time keeping the acyl content within a range to permit satisfactory rigidity and tensile strength. For manufacture of plastics, behavior toward plasticizers is a most important quality. Cellulose acetate requires comparatively high concentrations of active plasticizers for injection-molding operation, and those plasticizers which produce satisfactory flow characteristics are not retained as well as desired.[81] Here the mixed esters, particularly cellulose acetate butyrates containing a substantial amount of butyryl, offer distinct improvement since at the same time they possess greater compatibility with plasticizers which show better retention characteristics and they exhibit suitable flow with very small plasticizer concentrations. A cellulose acetate molding composition containing 49 parts of diethyl phthalate may thus be duplicated in flow characteristics by a cellulose acetate butyrate of 13% acetyl and 37% butyryl content with 15 parts of diamyl phthalate, the latter composition being much more permanent and dependable (Table 3).

The wider choice of volatile solvents for lacquers and film-forming solutions offered by mixed esters is, for many uses, an important factor. Esters, higher ketones, and mixtures of toluene with alcohols are among the common solvents which are most desirable for use, and which for cellulose acetate have been restricted because of solubility limitations. Fully esterified mixed esters are particularly desirable for some purposes. Exposure to high temperatures or to severe weather conditions is more damaging to hydrolyzed products than to those highly esterified, probably due to free hydroxyl groups being more susceptible to air oxidation than those protected by acyl groups. Reinhart and Kline[82] have found that a small amount of hydrolysis is desirable in cellulose mixed esters used for aircraft fabrics because of the more desirable effect of solvent mixtures on the physical properties of the products. Completely esterified esters became brittle upon exposure, while those with 0.2 to 0.4 free hydroxy group for each glucose unit withstood exposure tests exceptionally well. Higher free hydroxyl group contents gave greater tautness fluctuation causing coated fabrics to become slack in rain.

Esters of higher aliphatic, substituted aliphatic and aromatic acids, and mixed esters of these acids with lower aliphatic acids have received considerable attention, especially in patent literature. Products with very

[81] C. R. Fordyce and L. W. A. Meyer, *Ind. Eng. Chem.*, **32**, 1053 (1940).

[82] F. Reinhart and G. M. Kline, *Ind. Eng. Chem.*, **32**, 185 (1940).

PROPERTIES OF CELLULOSE ACETATE (38.5% ACETYL) VERSUS CELLULOSE ACETATE BUTYRATE (37% BUTYRYL, 13% ACETYL) PLASTICS (FORDYCE AND MEYER[81])

	Dimethyl Phthalate						Diethyl Phthalate					
	Cellulose acetate			Cellulose acetate butyrate			Cellulose acetate			Cellulose acetate butyrate		
Parts plasticizer per 100 parts base	37.8	30.0	22.6	15.8	11.0	6.3	59.5	49.0	38.7	17.0	12.0	7.0
Flow temp., °F	266	285	307	266	285	307	266	285	307	266	285	307
% Elongation	8.0	6.5	5.0	23.8	22.7	21.8	40.0	28.6	20.8	26.2	24.7	23.4
Tensile strength, lb./sq. in.	6,630	8,100	9,930	4690	5520	6,540	2860	3850	5100	4410	5340	6,470
Flexural strength, lb./sq. in.	11,140	14,200	17,000	7840	9240	10,950	3930	6050	8800	7390	8920	10,800
Rockwell hardness, M	79.5	90.5	101.1	72.4	80.1	86.4	49.0	59.7	75.5	65.5	75.2	84.3
% Water absorption (48 hrs.)	2.13	2.47	3.24	1.45	1.58	1.68	1.78	2.13	2.38	1.40	1.48	1.82
% Leaching (48 hrs.)	0.58	0.52	0.45	0.41	0.29	0.22	2.18	1.11	0.52	0.33	0.27	0.20
% Loss in wt. (1 wk. at 150°F.)	2.40	0.86	0.53	1.06	0.60	0.46	6.67	3.85	1.96	0.54	0.40	0.21
% Shrinkage (1 wk. at 150°F.)	1.38	0.11	0.09	0.89	0.48	0.19	3.02	1.53	0.70	0.33	0.27	0.13

	Di(methoxyethyl) Phthalate						Diamyl Phthalate		
	Cellulose acetate			Cellulose acetate butyrate			Cellulose acetate butyrate		
Parts plasticizer per 100 parts base	62.5	51.3	39.6	18.5	13.2	7.8	21.5	15.0	8.3
Flow temp., °F.	266	285	307	266	285	307	266	280	307
% Elongation	49.2	33.3	25.0	28.9	26.7	24.6	37.6	30.5	26.6
Tensile strength, lb./sq. in.	2760	3700	4880	3710	4680	5,870	4220	5180	6,340
Flexural strength, lb./sq. in.	3670	5700	8390	6430	8240	10,480	6240	8080	10,330
Rockwell hardness, M	20.6	44.3	67.2	60.1	71.2	82.0	56.5	69.2	80.4
% Water absorption (48 hrs.)	2.64	2.90	3.23	1.58	1.73	1.79	1.22	1.35	1.83
% Leaching (48 hrs.)	1.98	1.62	0.51	0.26	0.20	0.15	0.20	0.18	0.14
% Loss in wt. (1 wk. at 150°F.)	0.41	0.34	0.23	0.19	0.17	0.13	0.51	0.43	0.34
% Shrinkage (1 wk. at 150°F.)	0.29	0.21	0.17	0.13	0.11	0.09	0.39	0.28	0.14

interesting properties have been described, but for economic reasons they have found no broad industrial application.

2. Other Aliphatic Esters

(a) *Unsaturated Esters*

Preparation of cellulose esters of unsaturated aliphatic acids requires in general the same processes used for the corresponding saturated acids. Certain exceptions exist, however, in cases in which the unsaturated linkage interferes with normal behavior of the esterifying acid. Acrylic and methacrylic acids are difficult to employ as esterifying agents because of the ease with which these materials polymerize. Maxwell[83] has reported the preparation of mixed esters by reaction of methacrylic anhydride with cellulose acetate in presence of sodium acetate at least equivalent in quantity to the methacrylic acid formed by the reaction.

Crotonic acid is more stable in the monomeric form than the acrylic compounds and may be employed in the form of its anhydride with a suitable acid catalyst. It is less reactive than butyric anhydride, making it necessary to employ quite vigorous catalytic agents to obtain satisfactory esterification products. Gault and Angla[84] have recommended methanesulfonic acid in comparatively large quantities as a catalytic agent. The products obtained may be hydrolyzed by addition of mixtures of acetic acid, alcohol, and water.

Mixed esters of crotonic and acetic acids may be more readily obtained than the ester of crotonic acid alone. Preparation of these materials is similar to that previously described for cellulose acetate butyrates with the exception that crotonic acid, being much less reactive than butyric, is introduced into the ester to a considerably lower degree than butyric acid under the same set of reaction conditions. A reaction mixture of such a proportion as to give 40–45% butyryl from butyric anhydride and acetic acid when employed with crotonic anhydride results in only 15–18% crotonyl in the cellulose ester.

Cellulose crotonates are stable under ordinary conditions and undergo no appreciable change in composition or in physical properties when stored at room temperature. At higher temperatures, however, or under the influence of ultraviolet light,[85] these esters are converted to insoluble products.

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[83] R. W. Maxwell, U. S. Patent 2,175,357 (Oct. 10, 1939).

[84] H. Gault and B. Angla, U. S. Patent 1,969,882 (Aug. 14, 1934).

[85] C. J. Malm and C. R. Fordyce, U. S. Patent 1,973,493 (Sept. 11, 1934).

Cellulose tricrotonate, when heated at 100°C. for 24 hrs. or exposed to strong ultraviolet light for a shorter period of time, becomes completely insoluble in all organic solvents. This conversion may be made considerably more sensitive by incorporation of small quantities of benzoyl peroxide in the cellulose ester. This transformation is somewhat more sensitive in cellulose tricrotonate than in mixed esters containing smaller quantities of crotonyl but may be made to take place in cellulose acetate crotonates of considerably less than 10% crotonyl content.

Cellulose undecylinate has been prepared by Gault and Urban[86] by treatment of hydrocellulose with the acid chloride in the presence of toluene and pyridine at a temperature of 110–120°C. A product soluble in benzene was obtained.

Cellulose esters of higher-molecular-weight unsaturated acids such as oleic acid have been prepared by the use of chloroacetic anhydride as an impelling agent[87] and also by the reaction of the acid chloride in the presence of pyridine.[88] As in the case of esters of stearic acid, more interesting products are obtained in mixed esters such as may be prepared from acetone-soluble cellulose acetate by esterification of the free hydroxyl groups with the higher acids. Linoleic esters are considerably more sensitive to conversion to insoluble products than are those of oleic acid. Derivatives containing more than about 10% combined linoleic or linolenic acids become insoluble upon drying at ordinary temperatures. Interesting products result by esterification of cellulose acetate of 36–38% acetyl content with mixtures of stearic and linoleic acids.[89] The use of chloroacetic anhydride is recommended for their preparation. Products containing 30–40% combined higher acids result, 10–20% of which may be unsaturated. If the proportion of unsaturated acid increases appreciably beyond this point, conversion to insoluble products may take place during the esterification reaction. This may be prevented by reaction in an inert atmosphere, such as carbon dioxide or nitrogen.[90] The resulting esters are very resistant to moisture, form flexible films, and upon drying at ordinary temperatures are converted to insoluble products which are almost completely unaffected by most organic solvents.

Mixed esters containing unsaturated groups have also been prepared by

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[86] H. Gault and M. Urban, *Compt. rend.*, **179**, 333 (1924).

[87] H. T. Clarke and C. J. Malm, U. S. Patents 1,690,620 (Nov. 6, 1928); 1,739,210 (Dec. 10, 1929).

[88] W. Carpmael, Brit. Patent 239,726 (Sept. 17, 1925).

[89] C. R. Fordyce and G. D. Hiatt, U. S. Patent 2,170,016 (Aug. 22, 1939).

[90] C. J. Malm and G. D. Hiatt, U. S. Patent 2,241,226 (May 6, 1941).

the reaction of lauryl and polyricinoleic acid chlorides in the presence of pyridine.[91]

(*b*) *Halogen Substituted Esters*

The most outstanding characteristic of this group of cellulose esters is their difficulty of preparation. Barnett[92] investigated the reaction of chloroacetyl chloride on cellulose in presence of tertiary organic bases and was able to obtain only degraded derivatives. The procedure is complicated by side reactions of the halogen acid with the nitrogen base. Rudy[93] also obtained only badly degraded chloroacetyl esters by reaction of chloroacetic anhydride upon cellulose with an acid catalyst. Similar behavior resulted using anhydrides of di- and tri-chloroacetic acid. The reluctance of substituted acetic acids to esterify cellulose is unexplained. It is this characteristic behavior which has made possible their use as impelling agents to bring about esterification of other carboxylic acids.[3] Halogenated acids of more than five carbon atoms show less reluctance to react with cellulose than the lower members, giving esters in the normal manner. Thus, α-halogen stearic acids readily esterify cellulose or its derivatives containing free hydroxyl groups when reacted in presence of chloroacetic anhydride.[94]

Treatment of cellulose acetate with phosphorus pentachloride has been proposed as a method of replacing the hydrogen atoms of the acetyl groups by chlorine.[95] Minor quantities of chloroacetyl groups may also be introduced into cellulose acetate by hydrolysis of the acetate in chloroacetic acid solution, under which conditions the interchange of acyl groups takes place.

Esters of dihalogen acids may be made by addition of chlorine or bromine to the ethylenic groups of unsaturated cellulose esters. This is best accomplished in chloroform or tetrachloroethane solution.[96] Cellulose crotonate may in this way be readily converted to the 2,3-dihalogen butyrate and cellulose oleate to the 9,10-dihalogen stearate. The products are more widely soluble in organic solvents than the corresponding unsaturated esters, and by virtue of their high halogen content are much less flammable.

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[91] M. Hagedorn, U. S. Patent 1,966,757 (July 17, 1934).
[92] W. L. Barnett, *J. Soc. Chem. Ind.*, **40**, 253T (1921).
[93] H. Rudy, *Cellulosechem.*, **13**, 49 (1932).
[94] H. T. Clarke and C. J. Malm, U. S. Patent 1,698,049 (Jan. 8, 1929).
[95] I. G. Farbenindustrie Akt.-Ges., Brit. Patent 306,132 (Feb. 17, 1928).
[96] H. T. Clarke and C. J. Malm, U. S. Patent 1 687.060 (Oct. 9, 1928).

(c) *Hydroxy and Keto Esters*

The more common lower-molecular-weight hydroxy and keto acids, such as lactic, pyruvic, or acetoacetic acids, have not yet been successfully used to produce high degrees of esterification of cellulose. Hydroxy acids can not be employed in ordinary esterification procedures without at the same time esterifying the hydroxyl group. Alpha- and beta-keto acids are unstable in the presence of anhydrides or catalysts used for esterification. Higher keto acids, however, such as levulinic acid in which the keto group is beyond the beta position, may be used with the usual reaction methods employed for acids of comparable molecular weight.

Hydrolyzed cellulose esters containing minor quantities of combined hydroxy or keto acyl groups may be prepared by employing these acids as reaction media for hydrolysis of cellulose acetate.[97] This hydrolysis follows the behavior of equilibrium reactions, permitting a certain amount of interchange of acyl groups between the reaction solvent and the cellulose esters. This results in a proportion of the acyl groups from the hydrolysis solvent combining with cellulose as well as a continual removal of acyl groups from the cellulose ester. The reaction may be carried out in the presence of a catalyst at a moderate temperature or at higher temperatures with no added catalytic agent. Cellulose acetate lactates, tartrates, pyruvates, and citrates may be made in this way. Several of the products are soluble in water.

(d) *Alkoxy Acyl Esters*

Acid chlorides of alkoxy fatty acids may be made to react with cellulose in the presence of pyridine to give soluble products, although there is usually difficulty in obtaining complete esterification. Cellulose derivatives with free hydroxyl groups may be quite readily esterified by reaction of either the acid chlorides or anhydrides of these acids in pyridine.[98]

In the presence of acid catalysts, anhydrides of alkoxy acetic acid are similar to halogen-substituted acetic acids in that they do not react to give cellulose derivatives. For this reason they may be employed similarly to chloroacetic anhydride as impelling agents to form esters of other organic acids.[5] Similar to hydroxyacetyl groups, small amounts of alkoxy acyl groups can be introduced by hydrolyzing a cellulose ester using an alkoxy fatty acid as solvent.

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[97] C. J. Staud and C. S. Webber, U. S. Patent 1,900,871 (Mar. 7, 1933).

[98] C. J. Malm and J. D. Coleman, U. S. Patent 2,028,792 (Jan. 28, 1936).

3. Miscellaneous Esters

(a) *Aromatic Acid Esters*

There has been no commercial interest in cellulose esters of aromatic acids, investigation of their properties having shown no advantages of importance over the more readily prepared aliphatic esters. Cross and Bevan,[99] in the course of their researches on cellulose, prepared esters of benzoic acid by reaction of the acid chloride on alkali cellulose. Incomplete esterification was obtained, lower concentrations of reagents giving a fibrous monobenzoate, while under more severe reaction conditions a solution of the dibenzoate resulted.

Cellulose tribenzoate was prepared by Wohl using an excess of benzoyl chloride in pyridine at 110–130°C. with nitrobenzene[100] as a diluent. A modification of this process has been patented by Webber and Staud[101] in which bis(2-chloroethyl) ether instead of nitrobenzene is used as a reaction diluent. Ost and Klein[102] investigated both caustic alkali and pyridine as reaction media for benzoylation. A basic pyridine reaction mixture was recommended as most satisfactory, giving products of 73% combined benzoic acid.

Atsuki and Shimoyama[103] prepared cellulose dibenzoate from both normal and regenerated cellulose. After treatment with 35% alkali, the cellulose was aged 24 hrs. at ordinary temperature, then reacted with a benzene solution of benzoyl chloride at 50–60°C. for 1–2 hrs. The product from regenerated cellulose was completely soluble in chloroform and acetone, while that from normal cellulose gave poor solutions.

Benzoic acid in presence of chloroacetic anhydride reacts to give cellulose tribenzoate. A recommended procedure is the reaction of 3 parts of cotton, 15 parts of benzoic acid, 20 parts of chloroacetic anhydride, and 0.05 part of magnesium perchlorate for 8 hrs. at 60–70°C. The same reaction conditions may be employed for various substituted acids, including chloro-, nitro-, and methoxy-benzoic acids. The nitro- and halogen-substituted acids react more difficultly than benzoic; the methoxy derivative is readily

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[99] C. F. Cross and E. J. Bevan, *Researches on Cellulose, 1895–1900*. Longmans, Green, London, p. 34.

[100] A. Wohl, *Z. angew Chem.*, **25**, 285 (1903).

[101] C. S. Webber and C. J. Staud, U. S. Patent 1,831,274 (Nov. 10, 1931).

[102] H. Ost and F. Klein, *Z. angew Chem.*, **26**, 437 (1913).

[103] K. Atsuki and K. Shimoyama, *Cellulose Ind.* (Tokyo), **2**, 336 (1926); *Kunstseide*, **10**, 250 (1928).

esterified.[104] Cellulose cinnamate has been prepared both by reaction of the acid chloride in presence of pyridine[105] and by esterification with the acid in presence of chloroacetic anhydride.[3]

Phenylacetyl chloride, when reacted upon cellulose in a mixture of pyridine and chlorobenzene at 80–120°C., yields an ester of 77% combined phenylacetic acid, which melts at 140°C.[74]

(*b*) *Dibasic Acid Esters*

Cellulose may be esterified by either one or both carboxyl groups of dibasic acids. Products of the latter type, such as are obtained by treatment of a pyridine solution of hydrolyzed cellulose acetate with a dibasic acid

TABLE 4

PROPERTIES OF CELLULOSE ALKYL ESTERS OF DIBASIC ACIDS (MALM AND FORDYCE[106])

Cellulose ester	M. p., °C.	Solubility in:							
		Acetone	Methyl ethyl ketone	Ethyl acetate	Butyl acetate	Ethylene dichloride	Benzene	Toluene	Dioxane
Methyl succinate	195	+	+	+	−	+	−	−	+
Ethyl succinate	128	+	+	+	−	+	+	−	+
Propyl succinate	108	+	+	+	+	+	+	+	+
Butyl succinate	106	+	+	+	+	+	+	+	+
Methyl phthalate	180	+	+	+	−	+	−	−	+
Ethyl phthalate	178	+	+	+	+	+	+	−	+
Propyl phthalate	175	+	+	+	+	+	+	+	+
Butyl phthalate	155	+	+	+	+	+	+	+	+

Key: + soluble; − insoluble.

chloride, are insoluble in all solvents, indicating three-dimensional linkages, and the products are of comparatively little interest. If only one carboxyl group is combined with cellulose, the other may either be esterified by some other organic radical or remain in the free acid form. Products of both types have been made.

[104] H. T. Clarke and C. J. Malm, U. S. Patent 1,704,283 (Mar. 5, 1929); Brit. Patent 313,408 (Aug. 27, 1929); Societé Kodak-Pathé, French Patent 653,742 (Dec. 31, 1929).

[105] G. Frank and H. Mendrzyk, *Ber.*, **63B**, 875 (1930).

[106] C. J. Malm and C. R. Fordyce, *Ind. Eng. Chem.*, **32**, 405 (1940).

Frank and Caro[107] prepared cellulose oxalic acid esters by reaction of acid chlorides of half esters of oxalic acid with cellulose in presence of pyridine, using nitrobenzene as a diluent. The lower alkyl cellulose oxalates were found to be widely soluble in organic solvents, while the cetyl ester was more limited, and the menthyl ester only partly soluble in all solvents.

Similar products may be prepared by reaction of the acid form of the half esters with cellulose using chloroacetic anhydride as an impelling agent.[108] Cellulose alkyl succinates and phthalates have melting points below 200°C. and are soluble in a wide variety of solvents[106] (Table 4). Mixed esters prepared by esterification of the free hydroxyl groups of hydrolyzed cellulose acetate with dibasic half esters also show wide solubilities (Table 5) and exhibit better film-forming properties than the single esters.

TABLE 5

PROPERTIES OF CELLULOSE MIXED ESTERS CONTAINING ALKYL DICARBOXYL GROUPS (MALM AND FORDYCE[106])

Ester of cellulose acetate with:	M. p., °C.	Solubility in:									
		Acetone	Methyl ethyl ketone	Ethyl acetate	Butyl acetate	Ethylene dichloride	Benzene	Toluene	Benzene: alcohol, 2:1	Toluene: alcohol, 2:1	Dioxane
Methyl succinate	195	+	+	+	−	+	−	−	−	−	+
Benzyl succinate	175	+	+	+	−	+	−	−	−	−	+
Methyl phthalate	175	+	+	+	+	+	−	−	+	−	+
Ethyl phthalate	...	+	+	+	+	+	−	−	+	+	+
Butyl phthalate	168	+	+	+	+	+	+	+	+	+	+

Key: + soluble; − insoluble.

Cellulose half esters of dibasic acids, with the second carboxyl group in the acid form, are best prepared by reaction of dibasic acid anhydrides in presence of tertiary organic bases.[109] Cellulose or its derivatives containing free hydroxyl groups are heated on a steam bath with an excess of the dibasic acid anhydride and sufficient pyridine to form a viscous solution of the reaction product. The resulting solution of the pyridine salt may be

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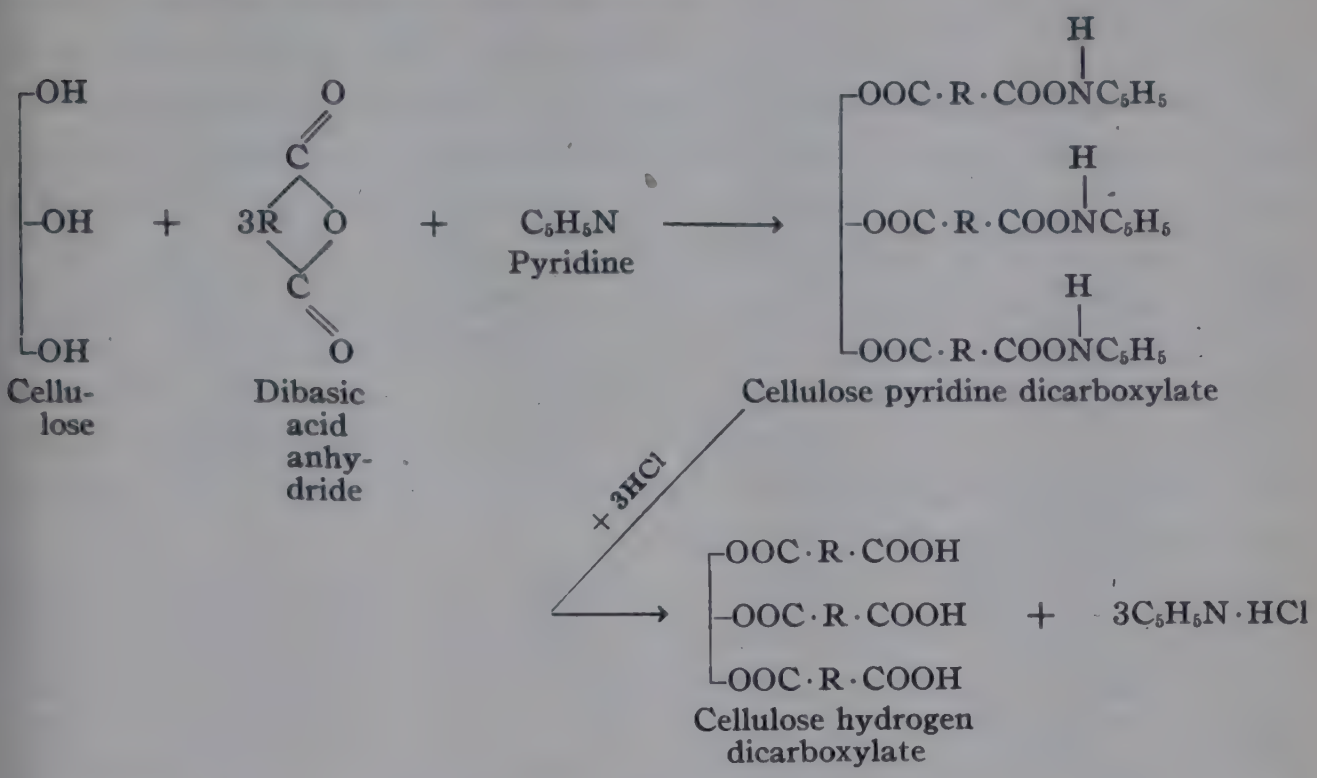
[107] G. Frank and W. Caro, *Ber.*, **63B**, 1532 (1930).

[108] R. L. Stinchfield, U. S. Patent 1,704,306 (Mar. 5, 1929).

[109] C. J. Malm and C. R. Fordyce, U. S. Patent 2,024,238 (Dec. 17, 1935); F. Schulze, U. S. Patent 2,069,974 (Feb. 9, 1937); C. J. Malm and C. E. Waring, U. S. Patents 2,093.462 (Sept. 21, 1937); 2,093,464 (Sept. 21, 1937).

precipitated as the free acid by water acidified with an excess of mineral acid. The reaction follows the equation:



Products of somewhat lower viscosity may be made without the use of pyridine by heating cellulose acetate and dibasic anhydrides at higher temperatures in a neutral solvent.[110]

The acid dicarboxylates, such as cellulose succinate or phthalate, are very

TABLE 6

PROPERTIES OF CELLULOSE ACETATE PHTHALATES OF VARYING PHTHALYL CONTENT (MALM AND FORDYCE[106])

Phthalyl content, %	M. p., °C.	Solubility in:											
		Acetone	Methyl ethyl ketone	Ethyl acetate	Butyl acetate	Ethylene dichloride	Benzene	Toluene	Benzene: alcohol, 2:1	Toluene: alcohol, 2:1	Dioxane	Dilute NH_4OH	Dilute NaOH
10	243	+	+	+	−	+	−	−	−	−	+	−	−
15	211	+	+	+	−	+	−	−	+	−	+	−	+
20	201	+	+	+	−	−	−	−	+	−	+	+	+
35	178	+	+	+	−	−	−	−	+	+	+	+	+

Key: + soluble; − insoluble.

[110] L. B. Genung, U. S. Patent 2,126,794 (Aug. 16, 1938); L. Blanchard and C. Crane U. S. Patent 2,183,982 (Dec. 19, 1939).

limited in solubility in organic solvents, but readily dissolve in dilute ammonia or sodium hydroxide. Mixed esters prepared from hydrolyzed cellulose acetate become increasingly soluble in organic solvents with increasing content of combined dibasic acid (Table 6). Products of more than about 25% of phthalyl or succinyl groups are comparatively moisture resistant in the acid form, and are readily converted to water-soluble salts by dilute basic solutions.[111] Viscous aqueous solutions of the sodium salts may be prepared by suspending the cellulose ester in water and adding small quantities of sodium bicarbonate with stirring until a uniform solution is obtained.[112] Organic bases such as the ethanolamines may also be used to prepare aqueous solutions.[113] With heavier metals, these cellulose derivatives give salts insoluble in water. These may be precipitated from an aqueous solution of the sodium salt by addition of an excess of a suitable water-soluble salt of the heavy metal.[114]

The acid esters are useful for application of water-insoluble surface coatings or sizings which are later to be removed by treatment with dilute aqueous alkali. They have been suggested for enteric coatings for medical purposes,[115] since they are resistant to conditions encountered in the stomach but are soluble in the more alkaline medium of the intestinal tract.

(*c*) *Sulfonic Acid Esters*

Cellulose may be esterified by acid chlorides of organic sulfonic acids either in presence of alkali or tertiary organic bases. Under acid conditions of reaction, the sulfonic acids do not esterify cellulose; they are, on the other hand, suitable catalysts for certain esterification procedures.

Most published work on these derivatives has been concerned with esters of toluenesulfonic acid. Sakurada and Nakashima[116] studied the reaction of alkali cellulose with *p*-toluenesulfonyl chloride, obtaining best results at temperatures under 30°C. The degree of esterification for a single treatment corresponded to somewhat less than a monoester, although, by repeated esterification, products between mono- and di-esters were obtained.

Hess and Ljubitsch,[117] using pyridine as a reaction medium, obtained a

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[111] C. J. Malm and C. E. Waring, U. S. Patent 2,093,463 (Sept. 21, 1937).

[112] C. J. Malm and C. R. Fordyce, U. S. Patent 2,082,804 (June 8, 1937).

[113] C. R. Fordyce, U. S. Patent 1,969,741 (Aug. 14, 1934).

[114] C. J. Malm and C. R. Fordyce, U. S. Patent 2,040,093 (May 12, 1936).

[115] G. D. Hiatt, U. S. Patent 2,196,768 (Apr. 9, 1940).

[116] I. Sakurada and T. Nakashima, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), 6, 214 (1927).

[117] K. Hess and N. Ljubitsch, *Ann.*, **507**, 62 (1933).

product containing 12% chlorine and 1% nitrogen from reaction at 70°C. By use of cuprammonium rayon as a starting material and reaction at 15–20°C., an ester containing two tosyl groups for each glucose unit and only 0.2% chlorine and 0.7% nitrogen was obtained.

Bernoulli and Stauffer[118] attempted to avoid the side reactions by using the anhydride of toluenesulfonic acid in pyridine under a variety of conditions but obtained only a minor degree of esterification.

Rigby[119] has described a modified method for reaction of *p*-toluenesulfonyl chloride on alkali cellulose, employing first a temperature not above 20°C., then an elevated temperature up to 120°C. Esterification corresponding to 1.5 to 1.7 tosyl groups for each glucose unit is obtained. Large quantities of tosyl chloride and alkali are necessary.

Malm and Nadeau[120] have patented the preparation of mixed esters by reaction of cellulose derivatives containing free hydroxyl groups with aromatic sulfonyl chlorides in presence of pyridine. The products have improved solubilities in organic solvents and are highly resistant to moisture.

The chemical properties of cellulose toluenesulfonic esters are of special interest. Cramer and Purves[121] have shown that the tosyl group reacts most readily with the primary hydroxyl group of the cellulose, esterification beyond that point being at a considerably slower rate. The primary and secondary hydroxyl groups are distinguished by the selective reaction of sodium iodide in acetone solution replacing tosyl groups on primary hydroxyls by iodine. Secondary tosyl esters remain unchanged. By preparation of tosyl derivatives of acetone-soluble cellulose acetate and treatment with sodium iodide, it was found that, of the free hydroxyl groups in the cellulose acetate, at least one-third were primary.

Modification of the dyeing properties of cotton through introduction of tosyl groups followed by treatment with ammonia or amines was suggested by Karrer and Wehrli,[122] since the tosyl radical is replaced by amino groups.

Hess and Ljubitsch, by treatment of ditosyl cellulose with ammonia or ethylamine, were not able to introduce over 2% nitrogen. Treatment of cellulose sulfonic esters with aliphatic primary or secondary amines to produce derivatives soluble in dilute acid has been patented by Haskins.[123]

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[118] A. L. Bernoulli and H. S. Stauffer, *Helv. Chim. Acta*, **23**, 627 (1940).
[119] G. W. Rigby, U. S. Patent 2,123,806 (July 12, 1938).
[120] C. J. Malm and G. F. Nadeau, U. S. Patent 2,036,423 (Apr. 7, 1936).
[121] F. B. Cramer and C. B. Purves, *J. Am. Chem. Soc.*, **61**, 3458 (1939).
[122] P. Karrer and W. Wehrli, *Z. angew. Chem.*, **39**, 1509 (1926).
[123] J. F. Haskins, U. S. Patent 2,136,299 (Nov. 8, 1938).

It is necessary to carry out the reaction in solution, preferably employing the amine to be reacted as solvent. The reaction solution is allowed to stand at 20 to 65°C. for several days, yielding products which may contain from 0.5 to 1 amino group for each glucose unit. Amylamine appears to be a particularly useful reagent. The products obtained are insoluble in water but soluble in dilute acids which form amine salts. The cellulose derivatives may be reprecipitated by treatment with alkali.

Wolfrom, Sowden, and Metcalf[124] have prepared cellulose esters of methanesulfonic acid. Mercerized cotton and cellulose regenerated from the acetate as starting materials yielded products between the mono- and di-ester. They did not dissolve in the reaction mixture during preparation. Cellulose acetate of low acetyl content (1.7 acetyl groups) was reacted to introduce one mesyl group. This product, when treated with sodium iodide, resulted in a lower degree of iodine replacement than did tosyl derivatives, contrary to that which might be expected from behavior of hexoses. The mesyl derivatives were also comparatively inactive toward replacement by ammonia.

(*d*) *Carbamic Acid Esters*

Carbamates of cellulose may be prepared by reaction of isocyanates upon dry cellulosic material in the presence of tertiary bases. Phenyl isocyanate under suitable conditions reacts very readily with cotton linters or with cellulose derivatives containing free hydroxyl groups. Goissedet[125] prepared cellulose phenyl carbamate by treating cellulose with three times its weight of phenyl isocyanate in dry pyridine at 120°C. To improve the reaction conditions, the cellulose may be swollen in water and the water then replaced by pyridine[126] before esterification.

For modification of the properties of textile materials, conditions of reaction have been recommended[127] which give partial esterification without altering the fiber structure.

Esterification of the free hydroxyl groups of hydrolyzed cellulose acetate with isocyanates may be employed to produce products soluble in ordinary solvents such as acetone.[128]

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[124] M. L. Wolfrom, J. C. Sowden, and E. A. Metcalf, *J. Am. Chem. Soc.*, **63**, 1688 (1941).

[125] P. E. C. Goissedet, Brit. Patent 130,277 (July 31, 1919); U. S. Patent 1,357,450 (Nov. 2, 1920).

[126] I. G. Farbenindustrie Akt.-Ges., German Patent 544,777 (Feb. 22, 1932).

[127] Gesellschaft für Chemische Industrie, Basel, Swiss Patent 142,749 (Dec. 16, 1930).

[128] C. J. Malm and G. F. Nadeau, U. S. Patent 1,991,107 (Feb. 12, 1935).

Completely anhydrous reaction conditions are very important in esterification with isocyanates, since each molecular equivalent of water consumes two equivalents of the isocyanate in formation of urethanes. Phenyl carbamates are highly moisture resistant and are soluble in a variety of organic solvents. The phenyl carbamyl groups are exceptionally stable toward either acid or alkaline hydrolysis.

4. Methods of Analysis†

Most uses for cellulose esters require analytical data covering chemical composition, viscosity, and stability. Practical methods for making these tests are described in the following sections. In addition, numerous other measurements, such as solubility characteristics, moisture resistance, color, dielectric constant, and hardness, may be of importance for specific applications, but are outside the scope of this discussion.

(*a*) *Acyl Determination*

Esters of Monocarboxylic Acids.

Total Acyl Content. The total acyl contents of cellulose formates, acetates, acetate propionates, and acetate butyrates having not more than 35 to 40% propionyl and/or butyryl are readily determined by the modified Eberstadt method.[129] The sample, after swelling with warm 75% alcohol, is saponified about 48 hrs. at less than 35°C. using aqueous alkali with an initial concentration of 0.25 normal. The excess alkali is then slowly and carefully back, titrated with standard acid. Esters of higher aliphatic acids such as propionic, butyric, valeric, capric, and stearic may be analyzed by saponification with 0.25 normal alcoholic alkali[129] for 16 to 24 hrs. at less than 30°C. This method is rather widely applicable to cellulose esters, including esters of aromatic acids. The accuracy of this procedure is inferior to that obtainable by the Eberstadt method, so that the latter should be used when possible. Both of these methods involve heterogeneous saponifications, making the physical condition of the sample an important variable. Cellulose acetates and certain other esters can also be analyzed by the Ost distillation method[129] wherein the sample is decomposed using a 1:1 (by volume) sulfuric acid-water mixture, and the liberated acetic acid is steam distilled and titrated. This method is particularly useful in cases where the analysis must be made in the presence of alkali-consuming

† This section was prepared by Dr. Leo B. Genung, Eastman Kodak Company.

[129] L. B. Genung and R. C. Mallatt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 369 (1941).

nonvolatile groups. It is also possible to carry out the saponification of an ester in solution, and thereby eliminate the physical condition of the sample as variable. The solvent or mixture of solvents must be varied depending on the solubility of the ester being tested; also, the time, temperature, and strength of alkali must be kept within about the same limits as required by the other saponification methods.

Mixed Ester Analysis. Many of the common mixed esters, such as the acetate propionates and acetate butyrates, may be analyzed satisfactorily by the partition method,[130] which involves the following steps: determination of total combined acids by one of the above-described methods, saponification and isolation of a mixture of these combined acids; determination of the partition coefficients of the acid mixture between *n*-butyl acetate and water, and also separate measurement of the partition coefficients for each of the various acids present; calculation of the molar ratios of the acids using simultaneous equations; and calculation of the weight per cent of the acids, or combined acyl, from the molar ratios and the total acid content of the ester. This procedure is readily adaptable to esters of water-soluble acids, either volatile or nonvolatile. The accuracy attainable varies with the numerical differences in the partition coefficients of the component acids in the ester.

Mixed esters of the type of cellulose acetate stearate can be analyzed by measuring the total acid content by saponification with alcoholic alkali and a careful back-titration with standard hydrochloric acid. This same solution is then acidified with sulfuric acid, and the stearic acid is extracted with ether. The ether layer is washed with water to remove acetic acid, the ether evaporated off, and the residue of stearic acid then dissolved in alcohol and titrated. Acetic acid is calculated by difference. This method is satisfactory only when the two acids have widely separated solubilities in ether and in water.

Mixed esters in which one acid has a distinctive group, such as cellulose acetate chloroacetate, acetate nitrobenzoate, or acetate crotonate may be analyzed by measuring the total acidity by saponification, and then determining one acid by special means. For example, a chlorine analysis would show the amount of combined chloroacetyl, a nitrogen content could be calculated to nitrobenzoyl, and an unsaturated ester might be brominated and then analyzed for its bromine content. The other acid is then calculated by difference.

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[130] C. J. Malm, G. F. Nadeau, and L. B. Genung, *Ind. Eng. Chem., Anal. Ed.*, **14**, 292 (1942).

Esters of Dicarboxylic Acids. Dicarboxylic acid esters of cellulose, such as the phthalate, succinate, maleate, and mixed esters of these acids and acetic acid, are usually prepared in such a way that only one of the carboxyl groups is esterified and the second is free. Such esters can be analyzed by dissolving in a suitable neutral solvent mixture, such as pyridine with water, dioxane with water, or acetone and an alcohol plus water, and titrating with standard alkali, taking into account a blank on the reagents. Total acidity can be measured by one of the saponification methods, and, in the case of a mixed ester, the second component can be calculated by difference.

(*b*) *Free Hydroxyl Determination*

The free or unesterified hydroxyl groups in a cellulose ester may be measured directly by acetylation using a standard solution of acetic anhydride in pyridine.[131] The conditions of time of reaction, temperature, excess of reagent, and the technique of back-titrating the unused reagent must be carefully worked out, if accurate results are to be obtained.

(*c*) *Stability*

The stability of commercial cellulose esters is a property of considerable practical importance. Manufactured articles, such as cellulose acetate yarn, molded objects, and photographic film, must be stable toward heat and hydrolysis. Simple practical tests such as the following may be used to measure these properties:

Stability toward Heat.

(1) A sample is heated under standardized conditions and the color developed is then compared with a set of standards.

(2) The sample may be dissolved in a high-boiling solvent or plasticizer and then heated under standardized conditions. The color thus developed may be compared with a suitable set of standards.

(3) The loss (or retention) of viscosity during heating is another useful measure of the stability of a cellulose ester. One portion of the test sample is given a heat-treatment, and then both heated and unheated portions are dissolved in a suitable solvent. A comparison of the viscosities of these two solutions gives a direct measure of this property.

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[131] C. J. Malm, L. B. Genung, and R. F. Williams, Jr., *Ind. Eng. Chem., Anal. Ed.*, **14**, 935 (1942).

Stability toward Hydrolysis.

(1) A 10-g. sample is refluxed with 250 cc. of neutral distilled water for 24 hrs. using soda-lime tubes at the tops of the reflux condensers. After cooling and filtering, the filtrate or an aliquot is titrated with standard alkali. A blank or control is run in parallel and the indicated correction applied.

(2) Bergmann-Junk Test. A dry sample is heated in a special tube for 2 hrs. at 132°C. The contents of the tube are then washed out with distilled water and titrated with standard alkali, taking into account the titration for a blank run in parallel.

(*d*) *Viscosity*

Two or more different viscosities are usually required to characterize a cellulose ester.

Practical Viscosities. These viscosities are run on solutions of the ester in the solvent or solvent combination and at liquid-solid concentrations which duplicate or closely approximate the conditions under which the ester is to be used. This is necessary because both the fundamental viscosity of the ester and its solubility in the particular solvent used affect the viscosity, especially in concentrated solutions. It is often advantageous to measure also the variations of viscosity with concentration and with temperature, for small changes in these may produce large changes in viscosity.

Fundamental Viscosities. A useful measure of the degree of degradation of cellulose esters can be obtained by means of suitable viscosity measurements. These are made upon dilute solutions and in carefully chosen solvents in order to eliminate or at least minimize the effect of solubility on viscosity. Such viscosity data are dependent upon the molecular magnitude of the cellulose ester, and from them can be obtained information concerning the degree of polymerization or molecular weight of the sample under investigation.

Further details on viscosity are given in Sections E and F of Chapter IX.

D. ALKALI AND OTHER METAL DERIVATIVES

W. D. Nicoll and Rollin F. Conaway

The treatment of cellulose fibers with alkalies is one of the oldest and most important commercial reactions of cellulose. This broad field has been the subject of investigation by various workers for nearly 100 years, but still the full significance of Mercer's original experiments on the treatment of cotton fibers with aqueous solutions of alkalies, as well as Schweizer's observations on the solubility of cellulose in cuprammonium solution, is not fully understood. There are two important objectives in treating cellulose with alkalies, namely, to modify the physical and chemical properties of natural fibers such as in mercerization, and to obtain intermediates such as alkali cellulose for conversion to cellulose derivatives.

Due to the limited knowledge of the nature of the alkali metal-cellulose complexes, it is difficult to classify the different aspects of this field on a strictly chemical basis. The simplest and possibly the most useful classification is the following: alkali cellulose, the true metal alcoholates of cellulose, cuprammonium-cellulose complexes, and cellulose-organic base complexes. The organic nitrogen bases by definition are out of place in this chapter but are included since their action on cellulose is similar to that of the inorganic bases.

1. Alkali Cellulose

Strong alkali solutions acting on cellulose at low or normal temperatures produce alkali cellulose. This treatment of cellulose has been known by the textile industry for a very long time as "mercerization,"[1] so called after John Mercer who discovered the process in 1844.[2]

The technical use of alkali cellulose dates from the discovery of Lowe[3] in 1889 that tension increases luster, and from the even more important discovery of Cross, Bevan, and Beadle[4] in 1892 that treatment of alkali cellu-

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[1] D. A. Clibbens, *J. Textile Inst.*, **14**, T217 (1923).

[2] E. A. Parnell, *Life and Labors of John Mercer*. Longmans, Green, London, 1886.

[3] H. A. Lowe, Brit. Patents 20,314 (1889); 4452 (Dec. 22, 1890).

[4] C. F. Cross, E. J. Bevan, and C. Beadle, *J. Chem. Soc.*, **63**, 837 (1893).

lose with carbon disulfide produced cellulose xanthate which could be dissolved completely in water or dilute alkali to form an orange-yellow viscous solution which they termed "viscose." As a result of this discovery, the preparation of alkali cellulose, or "soda cellulose" as it is also often known, became the first step in the manufacturing operations of the important group of viscose industries from which modern civilization derives such varied products as rayon, transparent wrapping film, cellulose sponges, cellulose sausage casings, and certain types of bottle closures.

In addition to its use in the preparation of viscose, alkali cellulose is an important intermediate product in the preparation of certain cellulose ethers, such as the ethyl, methyl, and benzyl ethers, which find application in the preparation of films and many types of plastic products. Mercerization is also used in the preparation of certain types of highly absorptive papers and paperboard products now employed in the manufacture of such materials as shoe lasts and blotting papers. At present, however, the amounts of alkali cellulose going into these uses are relatively small in comparison with the hundreds of millions of pounds required in the manufacture of viscose. This discussion on the nature of alkali cellulose and its applications in industry will be presented, therefore, mainly from the standpoint of the viscose process.

(*a*) *Structure of Alkali Cellulose*

Mercer assumed that the formation of alkali cellulose is a result of chemical combination between the cellulose and sodium hydroxide, and that the resulting compound is susceptible to decomposition under the action of water. Karrer[5] in support of this view has cited analogous cases of simple and polyhydric alcohols and has pointed out that many of these alcohols form compounds of a characteristically complex nature with alkali. Other workers, however, have held that the changes involved when cellulose is treated with alkali are purely physical and similar to those produced in the swelling of many other colloidal substances. Emphasis in recent years has been given to the methods of x-ray analysis as a means of determining the changes occurring when alkali cellulose is formed, and this method of investigation appears to give definite support to the view that cellulose may form not only one, but possibly several, compounds with strong alkalies. The particular compound formed depends on the type of cellulose, the concentration of alkali in solution, and the temperature.

If a chemical compound is assumed as the more probable form for alkali cellulose, two opinions are possible. Either the cellulose, like the simple

[5] P. Karrer, *Cellulosechem.*, **2**, 125 (1921).

alcohols and certain other polyhydric compounds, forms a true alcoholate, that is, with a metal ion (M) substituting for a hydrogen atom, thus:

$$R_{cell}— OH + MOH \longrightarrow R_{cell}— OM + H_2O$$

or the alkali is present as an addition complex such as has been assumed to form between certain sugars and the alkali earth hydroxides. In the latter case, alkali cellulose would have the composition represented by $(R_{cell}—OH)_x \cdot (MOH)_y$. Although the literature indicates a considerable difference in opinion on this point, the majority of investigators in this field seem to agree that, at least in the presence of water, the addition complex is to be preferred over the alcoholate type of structure.

Another controversial point concerns the question of whether more than one addition complex may exist, with many investigators agreeing on $(C_6H_{10}O_5)_2 \cdot NaOH$ as correctly representing the composition of the alkali cellulose commonly formed in alkali solutions of 12 to 18% concentration. A second compound has been given the formula $C_6H_{10}O_5 \cdot NaOH$ and variously reported as existing in solutions containing 20 to 40% NaOH. X-ray evidence strongly supports the existence of a new crystalline structure in caustic soda solutions of about 21% concentration, but the results from other methods used in examining these compounds have not been consistent.

In this connection it should be kept in mind that different celluloses contain different ratios of crystalline to noncrystalline material. This affects the number of cellulose chains available for reaction, and, therefore, influences not only x-ray results but also those obtained by other methods.

Important reasons for the divergent views which have been expressed in regard to the structure of alkali cellulose include differences in the types of celluloses investigated, the colloidal nature of alkali cellulose, and the widely different concepts held in regard to the basic nature of the swelling process. Following the discovery of the preferential absorption of alkali by cellulose in contact with solutions containing more than 12% of sodium hydroxide, early investigators concentrated attention on this fact and tended to disregard swelling phenomena and the role played by water in the formation of alkali cellulose. More recently, it was recognized that considerable quantities of water accompany the alkali into the solid cellulose phase, and emphasis shifted to the ratio of water to the total amount of alkali present, as well as to the degree of swelling and accompanying increase in internal surface. For example, recent studies by Saito[6] have

[6] G. Saito, *J. Soc. Chem. Ind., Japan*, **43**, B126, B133, B160, B194 (1940); **44**, B89 (1941): *Cellulosechem.*, **18**, 106 (1940).

helped to clarify complex relationships existing between the total amounts of alkali and water absorbed and how these factors are influenced by such variables as the type of cellulose, the kind and concentration of alkali, the temperature, and even the addition of an inert substance such as sodium chloride. This and similar work will be discussed more in detail later, but, in general, support is given to the view that physical factors probably have a greater influence on the properties of alkali cellulose than does any stoichiometric relationship which may exist between cellulose and combined alkali.

Indeed, from the practical standpoint, it may be doubted whether the question of chemical compounds versus absorption is one that can be discussed profitably on its own merits. There is no doubt, however, as to the value of the exact knowledge of the quantitative relationships in the system cellulose–sodium hydroxide–water gained as a result of the immense amount of work inspired by the desire to explain the processes involved. For these reasons a brief review of the principal methods which have been used to study the problem seems justified.

(*b*) *Methods for Determining Alkali Absorbed*

The Direct Method. The first investigator to attempt to determine the amount of caustic soda taken up by cellulose was Gladstone,[7] who in 1852 treated cotton with various concentrations of sodium hydroxide and then washed the samples with cold absolute alcohol or hot alcohol of about 92.5% concentration until constant weight was obtained. Similar experiments were made with KOH, and Gladstone concluded that each of these alkalies forms definite compounds with the cellulose. The method of washing with alcohol has since been reinvestigated by several other experimenters who have used either the same or slightly improved modifications of Gladstone's original method. Rassow and Schwarze,[8] for example, found that results obtained by washing with alcohol depend to a great extent on the alkali content of the solution, the water content of the alcohol, and the selection of the proper indicator to determine the completion of the washing operation. The conclusion was reached that a compound containing 12.34 g. of NaOH per 100 g. of cellulose and corresponding to the formula $(C_6H_{10}O_5)_2 \cdot NaOH$ is formed in alkali solutions containing from 18 to 40% sodium hydroxide. Gladstone in his original work thought that this compound existed only in solutions containing less than

[7] J. H. Gladstone, *J. Chem. Soc.*, **5**, 17 (1852).

[8] B. Rassow and K. Schwarze, *Papier-Fabr.*, **28**, Tech.-wiss. Tl., 693, 746 (1930).

35% sodium hydroxide and that a second compound, $C_6H_{10}O_5 \cdot NaOH$, was formed in solutions of higher concentration. Rassow and Schwarze indicated that the latter result from Gladstone's work could be attributed to incomplete removal of the excess alkali as a result of using phenolphthalein as indicator to determine the end of the washing operation.

Bancroft and Calkin,[9] on the other hand, have criticized Gladstone's method, stating that it is not proof of compound formation since the use of alcohol only introduces another variable, and that the results merely indicate how much sodium hydroxide is retained by the sample under the conditions of washing used. If this conclusion is correct, it is surprising that the results obtained by Gladstone and certain other workers agree so well with those from at least two other methods, namely the change-in-titer and change-in-x-ray-diffraction-pattern, both of which have been interpreted to indicate the formation of a cellulose-alkali compound.

The Indirect or Change-in-Titer Method. The most widely studied method of determining the composition of alkali cellulose is that introduced by Vieweg[10] in 1907. It consists in determining by titration the change in alkali concentration when a known weight of cellulose is placed in either a known volume or known weight of alkali solution. This method, like the direct method of Gladstone, requires careful standardization of the experimental conditions in order to obtain reproducible results. Heuser and Niethammer[11] showed that the cellulose must be mercerized in a concentrated bath and recommended the use of 1 g. of cellulose in 10–12.5 g. of solution in order to obtain a consistent value for the alkali absorbed. The moisture content of the cellulose is also important and, according to Rassow and Schwarze,[8] absolutely dry cellulose must not be used as the absorption will then be nonuniform. Differences in results were also noted by Rassow and Schwarze[8] depending on the conditions of pressing off the excess liquor from the cellulose and on whether samples for titration were taken volumetrically or gravimetrically.

Probably the most persistent criticism which has been made of the indirect method is that made first by Leighton,[12] namely, that no attention is given to the very considerable swelling and hydration which occurs when cellulose is treated with strong solutions of alkali. This criticism, however, has generally been made by those interested in the total quantity of alkali

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[9] W. D. Bancroft and J. B. Calkin, *Textile Research*, **4**, 119, 159 (1934); *J. Phys. Chem.*, **39**, 1 (1935).

[10] W. Vieweg, *Ber.*, **40**, 3876 (1907); **41**, 3269 (1908); **57B**, 1917 (1924).

[11] E. Heuser and W. Niethammer, *Cellulosechem.*, **6**, 13 (1925).

[12] A. Leighton, *J. Phys. Chem.*, **20**, 32, 188 (1916).

absorbed by the cellulose and is not believed justified when only the preferentially absorbed alkali is to be determined. This point is further discussed below in connection with the work of Sharkov and Saito (p. 721).

The results obtained by use of the Vieweg indirect method may most readily be discussed by referring to the curve formed by plotting the apparent change in alkali absorption against the caustic soda content of the treating solution. This curve, generally known as the Vieweg curve,[13] has the following characteristics (Fig. 10). It shows a gradual increase in alkali absorption with increased concentration of caustic soda from 0 to

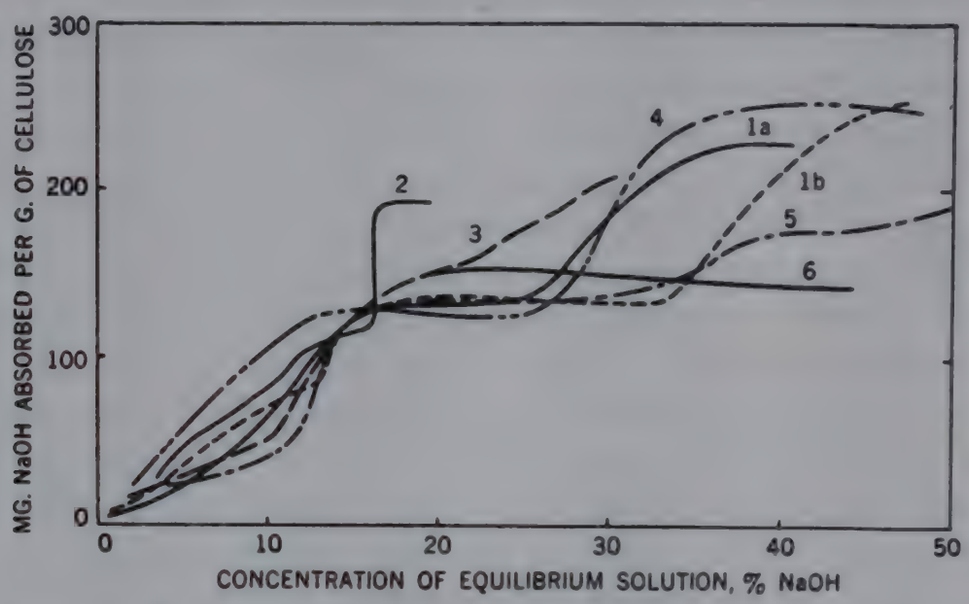

FIG. 10.—ALKALI PREFERENTIALLY ABSORBED BY CELLULOSE AS DETERMINED BY VARIOUS INVESTIGATORS USING THE CHANGE-IN-TITER METHOD (D'ANS AND JÄGER[13]).

Curves: 1a, Vieweg I; 1b, Vieweg II; 2, Liepatoff; 3, Rassow and Wadewitz; 4, Dehnert and König; 5, Heuser, Niethammer, and Bartunek; 6, Karrer and Nishida.

13–16% NaOH. At this point there occurs a definite break in the curve followed by a region of constant absorption up to a concentration of approximately 21% NaOH. Above this the curve again rises gradually but flattens off at a new level in the range of 35–40% NaOH. Richardson and Maass[14] made a study of the absorption of alkali from concentrated solutions, and, on the basis of their work and that of Rumbold[15] and Vieweg, constructed a curve which shows the absorption of alkali over the whole range of 0 to 50% concentration (Fig. 11).

The amount of alkali absorbed at the first break in the Vieweg curve has

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[13] J. d'Ans and A. Jäger, *Cellulosechem.*, **6**, 137 (1925).

[14] R. Richardson and O. Maass, *J. Phys. Chem.*, **36**, 3064 (1932).

[15] J. S. Rumbold, *J. Am. Chem. Soc.*, **52**, 1013 (1930).

been determined by different investigators and may be said to average about 13 g. of NaOH per 100 g. of cellulose. The absorption at the second break, when obtained, is approximately 22.5 g. of NaOH per 100 g. of cellulose. Vieweg, and many other investigators who have used the method more recently, concluded that the first break in the curve denoted the formation of a definite compound, $(C_6H_{10}O_5)_2 \cdot NaOH$, which is stable throughout the range of alkali concentration represented by the first flat portion of the curve. Evidence for the formation of the second compound, $C_6H_{10}O_5 \cdot NaOH$, in concentrations of caustic soda above 35% is not so clear, and several investigators following Vieweg were unable to obtain

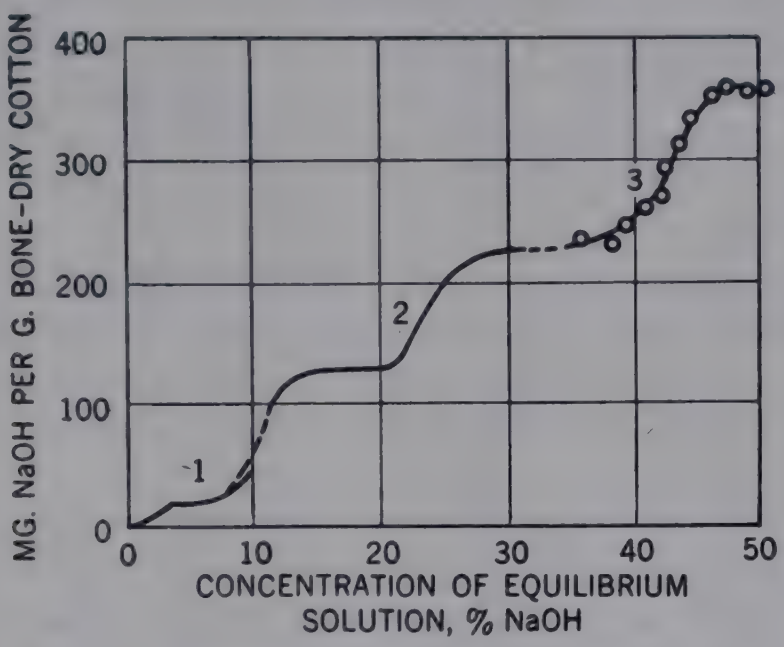

FIG. 11.—COMPOSITE CURVE FOR ALKALI PREFERENTIALLY ABSORBED BY COTTON AT 20°C. (RICHARDSON AND MAASS[14]).

Curves: 1, Rumbold; 2, Vieweg; 3, Richardson and Maass.

any absorption values sufficiently high to substantiate the existence of this compound.

The theory of compound formation and the use of the Vieweg method for determining alkali absorbed by cellulose has been vigorously attacked from a theoretical standpoint on the grounds that the curve does not conform to phase-rule requirements. Leighton[12] was the first to point this out, and it has since been discussed by Bancroft and Calkin.[9] According to these investigators, the alkali absorption curve should show a distinct vertical portion rather than a horizontal portion, as evidence for compound formation. As ordinarily determined, the curve does not show this, but rather

shows a gradual rise to the inflection point. An important factor not recognized by the critics of the Vieweg curve is that the system under investigation is one containing a high-molecular-weight material having characteristically colloidal properties. In such a system swelling is not uniform, and one should expect that as swelling progresses there would be a gradual increase in the amount of reactive surface available for compound formation and that this would preclude the possibility of obtaining a sharp vertical rise in the absorption curve. As is shown in Section A of this chapter, even if all of the cellulose chains are equally available, the extent of reaction will be a continuous function of the alkali concentration, and the alkali absorption curve will have the same shape as the titration curve of a polybasic acid if more than one type of addition complex of NaOH with cellulose is found. Calkin,[16] independently, later applied the x-ray method to the system and found that the change in x-ray diffraction diagram from native cellulose to that characteristic of alkali cellulose takes place only gradually, starting in a caustic soda solution of about 13% concentration and becoming complete at about 16% NaOH. This range, it will be recognized, coincides closely with that immediately preceding the break in the Vieweg curve. It seems likely, therefore, that the change in x-ray diffraction pattern and the gradual rise in the absorption curve for alkali may be due to one and the same phenomenon.

The Blotting or Centrifuging Method. Another method which has been widely used for investigating the cellulose–caustic soda–water system is to blot or to centrifuge off the excess alkali solution and to determine the total alkali and water taken up by the cellulose. Beadle and Stevens,[17] among the first to use the blotting method, studied particularly the effects of temperature and the concentration of the caustic soda solution. These experimenters used regenerated cellulose in the form of cuprammonium rayon, and their results (Fig. 12) show that, for temperatures between 5 and 40°C., points of maximum hydration and maximum alkali absorption occur, and that these maxima are greater with decrease in temperature. It may be seen that, for solutions of 3 to 9% alkali content, the effects of temperature on hydration and on caustic soda absorbed bear a close resemblance to each other (the shape of the curves are relatively much alike), indicating that under these conditions the solutions in which the cellulose was immersed were absorbed without change in composition. For the more concentrated solutions (10–25% NaOH) the curves are not similar,

[16] J. B. Calkin, *J. Phys. Chem.*, **40**, 27 (1936).

[17] C. Beadle and H. P. Stevens, *Orig. Com. 8th Intern. Congr. Appl. Chem.*, **13**, 25 (1912).

and this has been taken to mean that preferential absorption or chemical reaction occurred.

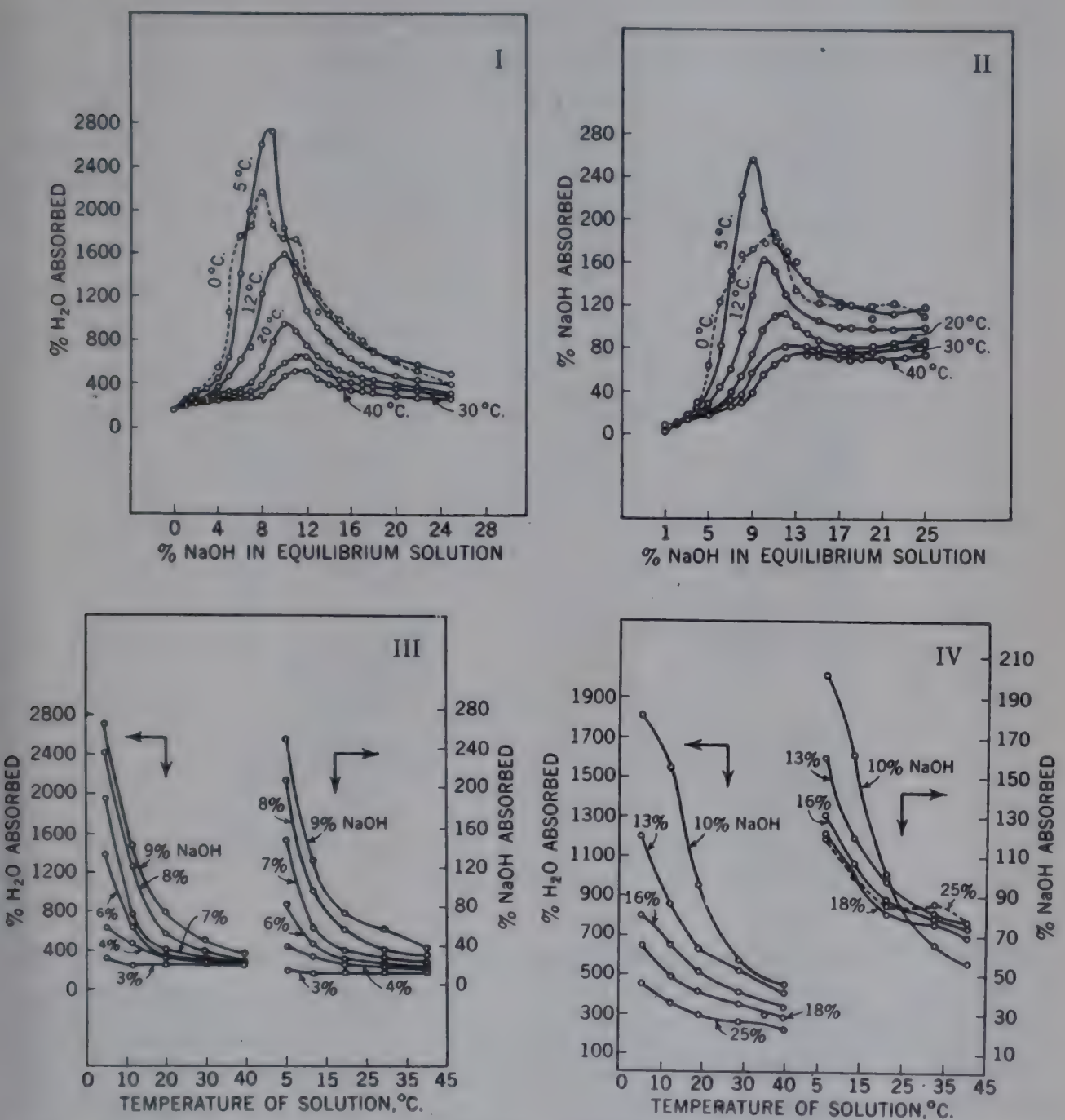

FIG. 12.—EFFECTS OF TEMPERATURE AND CONCENTRATION ON TOTAL ALKALI AND WATER ABSORBED BY REGENERATED CELLULOSE (BEADLE AND STEVENS[17]).

Neale[18] also employed the blotting method with small pieces of regenerated cellulose sheeting. His results (recalculated and graphically presented by Bancroft and Calkin) give the total quantities of sodium

[18] S. M. Neale, *J. Textile Inst.*, **20**, T373 (1929); **21**, T225 (1930); **22**, T320, T349 (1931).

hydroxide and water absorbed from solutions of varying concentrations. The maximum water absorption (600%) occurs at about 12% alkali concentration (Fig. 13). On close study it is found that, if the amounts of alkali preferentially absorbed as indicated by the Vieweg change-in-titer curve (Curve 2) are deducted from the total absorption (Curve 1), the remaining quantities of alkali and water are present in the cellulose in almost exactly the same proportions as in the mother liquors. The differences in total absorption may be assumed, therefore, to represent mainly differences in the degree of swelling.

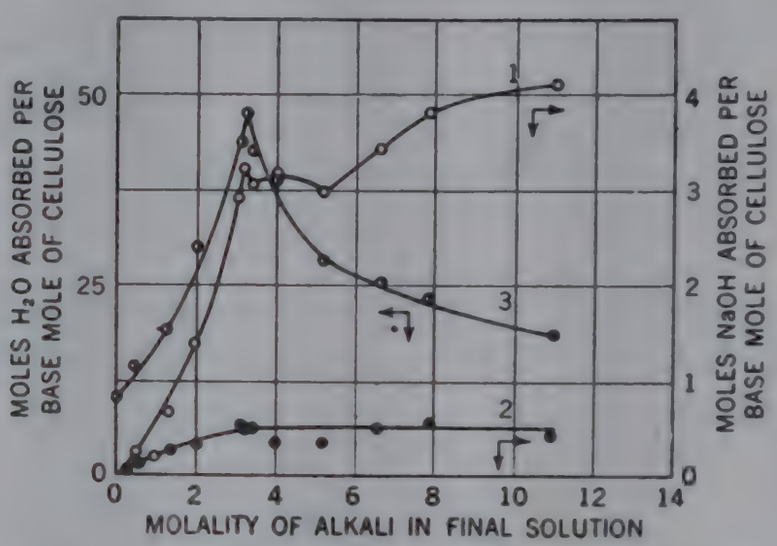

FIG. 13.—NaOH AND H_2O ABSORBED BY CELLOPHANE AT 25°C. (NEALE'S DATA RECALCULATED BY BANCROFT AND CALKIN[9]).

Curves: 1, total alkali absorbed; 2, preferentially absorbed alkali; 3, water absorbed.

Leighton[12] tried to determine the alkali absorbed by cellulose by using a centrifuge to remove excess alkali. The values he obtained produced a smooth absorption curve, and he concluded that no compound formation takes place. Coward and Spencer,[19] using a centrifuge of higher speed, determined carefully the efficiency with which the excess alkali could be removed. These workers concluded that in using a force equal to 2230 times gravity all but 5 to 10% of the excess alkali solution clinging to the surfaces of the fibers could be removed after $7^1/_2$ minutes of centrifuging. The centrifuged celluloses were analyzed to obtain the amount of alkali and water taken up.

Bancroft and Calkin[9] used the centrifuge method and determined in an indirect manner the point at which all the surface liquid was lost. Samples

[19] H. F. Coward and L. Spencer, *J. Textile Inst.*, **14**, T28, T32 (1923).

of the alkali cellulose taken progressively after various centrifuging intervals were analyzed and the results examined graphically by a special method which determined, by a change in the ratio of caustic soda to water leaving the cellulose, the point at which no more excess liquid remained on the surface. These authors concluded that the absorption of

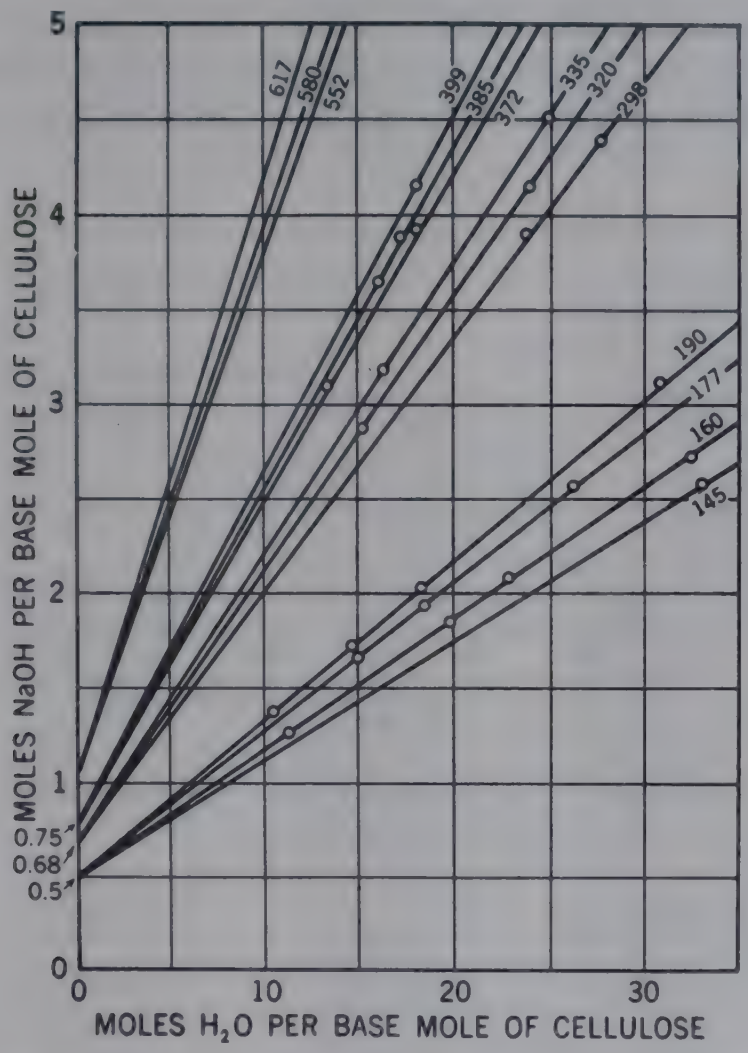

FIG. 14.—CHANGES IN THE COMPOSITION OF THE RESIDUES OBTAINED BY CENTRIFUGING TO DIFFERENT DEGREES THE ALKALI CELLULOSES PRODUCED IN NaOH SOLUTIONS OF VARIOUS CONCENTRATIONS (CHAMPETIER[20]).

The numbers on the curves represent the grams of alkali per liter.

alkali by cellulose is a purely physical phenomenon and that no chemical compounds are formed.

Champetier[20] also used the centrifuge method, but, instead of determining the total alkali absorbed, he used the values obtained by analyzing the alkali celluloses after progressive centrifuging to determine the quantity of preferentially absorbed alkali (Figs. 14 and 15). He did this by plotting

[20] G. Champetier, *Ann. chim.*, **20**, 5 (1933).

the alkali-water ratio found for the samples examined and extrapolating these results to the zero axis for water. The conclusion reached by Champetier was that cellulose may form as many as four distinctly different compounds with sodium hydroxide, as indicated by the following formulas:

$$(C_6H_{10}O_5)_2 \cdot NaOH;\ (C_6H_{10}O_5)_3 \cdot 2NaOH;\ (C_6H_{10}O_5)_4 \cdot 3NaOH;\ (C_6H_{10}O_5) \cdot NaOH$$

Probably the most serious objection that can be made to Champetier's method is that the extrapolations are large and could be carried out equally well in such a manner as to show uniform increase in bound NaOH with concentration.

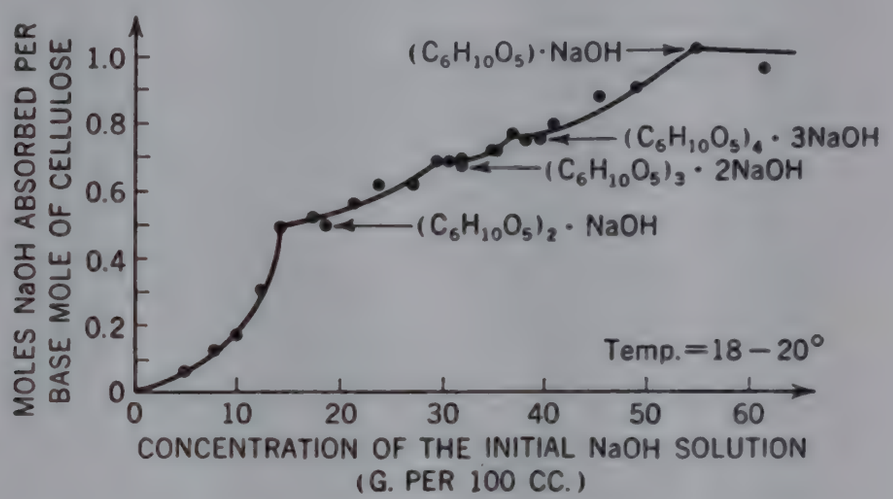

FIG. 15.—SODIUM HYDROXIDE PREFERENTIALLY ABSORBED BY CELLULOSE (CHAMPETIER[20]).

The Neutral Salt Method. Still another method used to study the formation of alkali cellulose, and more specifically to determine the amounts of water taken up by the cellulose, has been by the addition of a neutral salt such as sodium chloride to the alkaline treating solution. This method, originally used by Schwarzkopf,[21] is based on the assumption that if no salt is absorbed by the cellulose it should be possible to calculate the amount of water taken up by analyzing the mother liquor for chlorine before and after coming in contact with cellulose. Sharkov,[22] who also used this method, investigated its validity and concluded that it produced reasonable results provided the concentration of salt was low (1% or under). Bancroft and Calkin,[9] on the other hand, rejected the method as unsound, but there is a possibility that this may have been due to the fact that in their work they used too concentrated (5.0%) a solution of salt.

[21] O. Schwarzkopf, *Z. Electrochem.*, **38**, 353 (1932).

[22] V. I. Sharkov, *Iskusstvennoe Volokno*, **2**, 2 (1931).

Sharkov[22] and Saito[6] used the neutral salt method in conjunction with the Vieweg change-in-titer method to investigate the action of not only sodium hydroxide but lithium and potassium hydroxides as well. The data obtained do not agree absolutely but the general conclusions reached are similar.

Both Sharkov and Saito studied more than one cellulose and more than one alkali. Figure 16 shows data by Saito indicating that with sodium hydroxide there is a sharp increase in the amount of alkali absorbed by cellulose in the range of 2–4 *N* sodium hydroxide. Between this range and 6 *N* sodium hydroxide the absorption of alkali increases only very

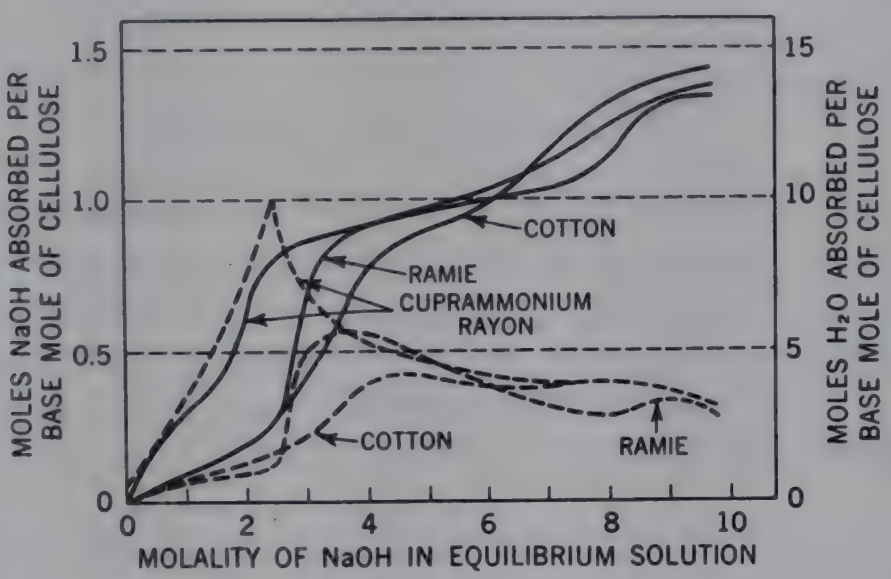

FIG. 16.—MINIMUM TRUE ABSORPTION OF NaOH AND H_2O BY DIFFERENT CELLULOSE FIBERS AT 20°C. (SAITO[6]).

——— Minimum NaOH absorption.
– – – – Minimum H_2O absorption.

slightly, but above 6 *N* the increase occurs again. Saito shows that, for the celluloses investigated, the absorption taking place in 6 *N* alkali is independent of the type of cellulose used and is approximately 1 mole of alkali per mole of cellulose. However, for lower concentrations of alkali, the amounts of sodium hydroxide absorbed vary considerably with the type of cellulose. Regenerated cellulose begins to absorb alkali strongly from solutions as weak as 2 *N*, similar absorption with ramie begins at about 3 *N*, and that for cotton at about 4 *N*. A similar situation holds for water absorbed, which, in the case of each cellulose, passes through a maximum, but the absorption of water by regenerated cellulose at the maximum is more than twice that reached by cotton.

One important difference to be noted between the results obtained by the sodium hydroxide-sodium chloride method and those obtained for water absorption by blotting off the excess alkali or centrifuging is that the total absorption (water + alkali) is only about half as great by the former as by the latter method. This difference may be explained if cellulose, in the form of films or fibers, can be assumed to have a porous structure capable of holding relatively large amounts of mother liquor which by the blotting method would be included along with any liquor more intimately associated with the cellulose itself. Presumably the same would not be true for water absorption determined by the neutral salt method, and one should therefore expect to obtain lower values by this method.

(*c*) *Swelling of Alkali Cellulose*

The physical swelling phenomena which all celluloses undergo when treated with a solution of an alkali hydroxide are theoretically fully as interesting and practically probably much more important than the purely chemical aspects of the changes involved in the formation of alkali cellulose. The two phenomena, chemical and physical, appear to be so completely interdependent that one cannot properly be considered without the other.

Mercer, in his study of the changes produced in cotton on treating with alkalies, observed generally the effects which swelling had on the luster, tensile strength, and dye affinity of the washed yarn. Crum,[23] in 1863, was the first to attempt a quantitative examination of the swollen condition of these fibers by measuring the cross section and determining the longitudinal shrinkage of cotton hairs. Crum introduced the use of the microscope as a tool for studying swelling and described in detail how the fibers lose their flat, ribbon-like form and assume a nearly cylindrical appearance.

The physical processes underlying the change in length and increase in diameter which a natural or artificial cellulosic fiber undergoes in alkali solutions are not definitely understood. On the basis of modern concepts concerning the fine structure of cellulose, these changes may be assumed to depend on the fact that the network of cellulose micelles is most highly oriented in the direction of the fiber axis. The alkali solution, entering between the micelles, pushes the units apart and loosens interconnecting secondary bonds which allows the structure to assume a less oriented condition. However, the rupture of the secondary bonds is probably incom-

[23] W. Crum, *J. Chem. Soc.*, **16**, 404 (1863).

plete, so that the structure is still held together at certain points, and the shape of the fiber must change anisotropically, that is, more in one direction than in the other.

Swelling differences observed in caustic solutions of varying concentrations can perhaps best be explained as either having inter- or intra-micellar character as first pointed out by Katz.[24] Since x-ray evidence indicates no change in spacing between individual cellulose chains when cellulose is brought into contact with solutions of caustic soda below 12% concentration, it may be assumed that in these solutions swelling takes place almost entirely between the micelles. Absorption of alkali solution is then entirely a result of osmotic forces acting between the water within the cellulose gross structure and the mother liquor. In solutions above 12% caustic soda concentration, the swelling process changes to the intramicellar type, since alkali is preferentially absorbed or combined with the cellulose and a definite change occurs in the crystal lattice as determined by x-rays.

In addition to the important factors of solution concentration and temperature, already mentioned as influencing the degree of swelling and alkali absorption, the following variables may also be considered when cellulose is treated with a solution of an alkali: (1) the nature of the cellulose, (2) the time of contact, (3) hysteresis and equilibrium, (4) changes in solvent, and (5) addition of salts.

Purified cotton or ramie cellulose is generally less readily swollen by alkalies than is either mercerized or regenerated cellulose. Wood pulps usually occupy an intermediate position. The differences in ability to swell appear to be associated with the degree of orientation and crystallinity of the cellulose chain molecules and micellar aggregates composing the various cellulose structures. In addition, one must also consider the previous history of the sample, such as treatments with hydrolyzing or swelling agents. To illustrate, Figure 16 shows typical data covering the swelling effects produced by different concentrations of sodium hydroxide on ramie, cotton, and regenerated cellulose. It will be seen that the regenerated cellulose both reaches a maximum in swelling at a lower concentration of alkali and swells much more highly than either of the native celluloses. The conclusion may be drawn that the ease and degree of swelling increases with diminishing structural organization of the cellulose.

Heuser and Niethammer[11] have reported that both hydro- and oxycellulose show an increase in degree of swelling and alkali absorption.

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[24] J. R. Katz, *Physik. Z.*, **25**, 321 (1924).

Neale[18] also studied the effects of alkali on degraded forms of cellulose but showed that, if these modified forms of cellulose are treated with hot dilute alkali, they lose their increased sensitivity toward swelling and alkali absorption and again behave as normal cellulose. The latter result is due, presumably, to removal of degraded celluloses present in the hydro- or oxy-celluloses.

The time of exposure to alkali is not a critical factor in the swelling of cellulose provided the cellulose is in the form of loose fibers or thin sheets. Under most conditions, mercerization and swelling take place almost instantaneously, but this is not necessarily true in the commercial viscose process where relatively thick sheets of pulp are generally used. Under the latter conditions, air may be entrapped between the fibers in the sheets, and it is important that it be expelled in order to obtain rapid and uniform swelling. In some cases, the use of certain surface-active agents has been proposed to promote better wetting of the cellulose. Particularly useful for this purpose are various mixtures of phenolic and hydroxy aliphatic compounds, several of which are described in the patent literature.

Neale's Theory of Swelling. Among the theories which have been advanced to explain swelling, one of the most interesting is that suggested by Katz[25] and Pauli and Valko,[26] and worked out by Neale.[18] According to this theory, the action of alkali on cellulose can best be represented as an osmotic effect. This is based on the assumption that cellulose may be regarded as a weak monobasic acid which forms a sodium salt approximately according to the laws of mass action. The reasons why a more exact adherence to the mass action laws is not obtained are three. First, the reacting system is not homogeneous, because it consists partially of crystallized and partially of amorphous materials, the whole mass being crisscrossed by submicroscopic, water-filled canals. Second, the cellulose molecule, being a high polymer, is polybasic, and it contains several different types of acid structures. Third, the alkalies used are in extremely high concentration, and the activities of the ions are no longer even roughly proportional to their concentrations. To help explain this theory Neale gives the following diagram:

$$\begin{array}{c} H\ \ Na^+\ H\ \ Na^+\ Na^+ \\ —A—A^-—A—A^-—A^-— \end{array}$$

in which A is the negatively charged unit or radical corresponding to each acid hydrogen atom. In dilute sodium hydroxide solution certain of these

[25] J. R. Katz, *Micellartheorie und Quellung der Cellulose*, in K. Hess, *Die Chemie der Zellulose*. Akademische Verlagsgesellschaft m.b.H., Leipzig, 1928.

[26] W. Pauli and E. Valko, *Electrochemie der Kolloide*. J. Springer, Wien, 1929.

hydrogens are replaced by sodium. The cations may be imagined as constantly moving along the network from point to point, replacing and being replaced by others, so that under given conditions a state of dynamic equilibrium is reached, the same total amounts of sodium ion, hydrogen ion, or undissociated cellulose hydroxyl groups being present at any one instant. Excess alkali may be thought of as diffusing into the cellulose in an amount determined by Donnan's thermodynamic equation for membrane equilibrium. The resulting unequal distribution of ions causes osmosis, imbibition of water, and swelling of the cellulose until the osmotic pressure is balanced by forces arising from the cohesion of the gel. On

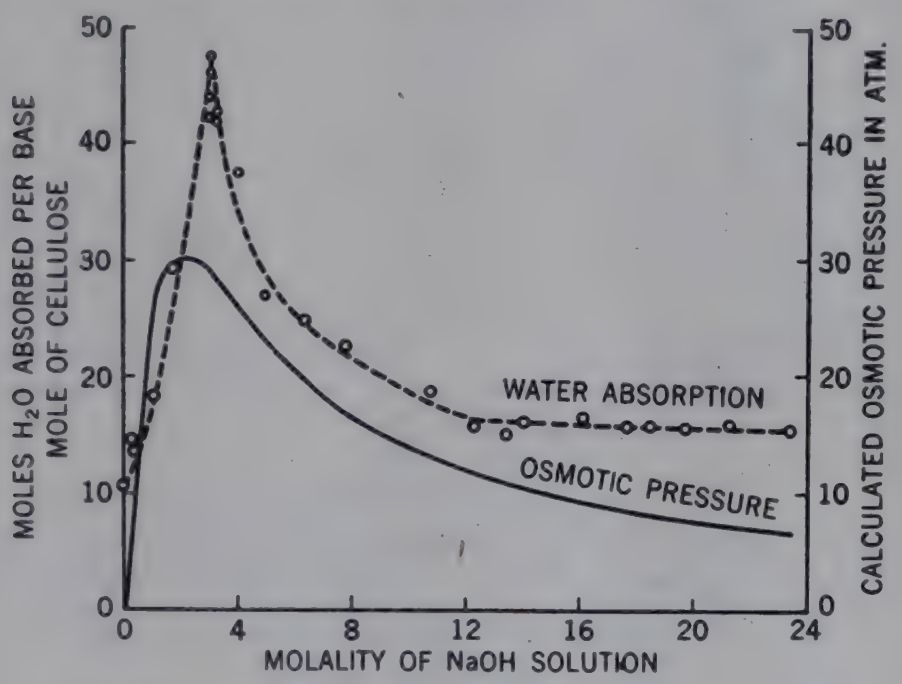

FIG. 17.—OSMOTIC PRESSURE AND WATER ABSORPTION OF CELLULOSE FILM (CELLOPHANE) FROM NaOH SOLUTIONS OF DIFFERENT CONCENTRATIONS (NEALE[18]).

washing with water, the cellulose sodium salt is hydrolyzed, the osmotic pressure falls, and the cellulose is recovered unchanged chemically but distorted physically by an amount depending upon the maximum osmotic pressure reached. The value 1.84×10^{-14} was determined as the ionization constant of the regenerated cellulose, and Neale calculated a theoretical osmotic pressure curve which was found to agree fairly well with the experimentally determined water absorption curve (Fig. 17). Neale, on the basis of this theory, was able to account for the greater swelling of cellulose in alkali solutions of intermediate concentration and also to explain why swelling is greater and the optimum concentration producing it lower for lower temperatures.

If cellulose is treated with a concentrated solution of alkali and then immersed in water or dilute alkali, it undergoes a transient swelling which is much greater than that produced by direct treatment with dilute alkali. Neale has explained this phenomenon on the basis of the osmotic pressure theory of swelling by assuming that the cellulose reaches an equilibrium with the concentrated alkali solution so that, if suddenly plunged into water, the sudden rise in osmotic pressure causes an imbibition of water by

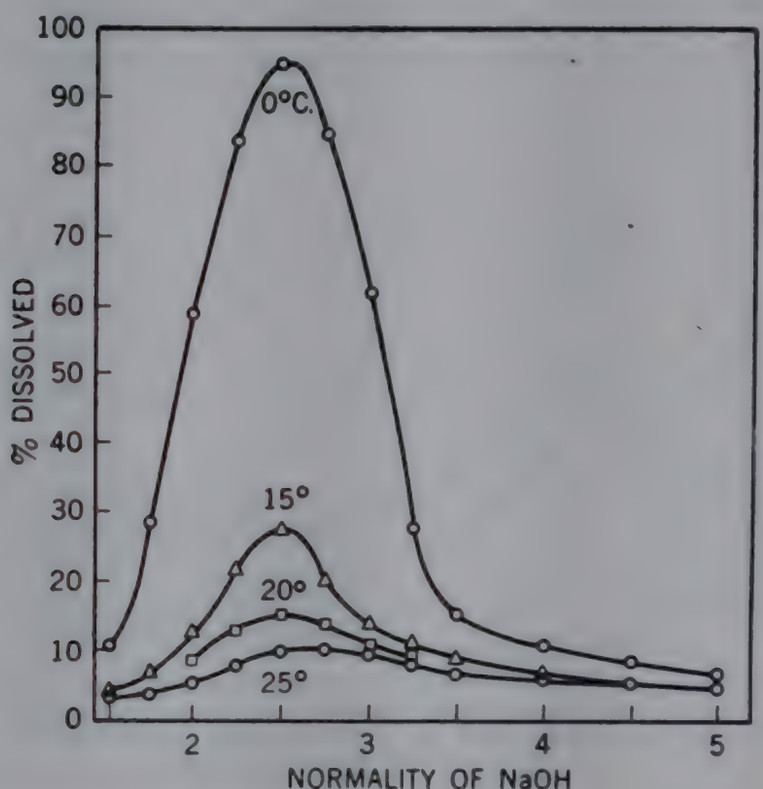

FIG. 18.—SOLUBILITY OF CELLOPHANE IN NaOH SOLUTIONS AT VARIOUS TEMPERATURES (DAVIDSON[27]).

the solid phase sufficient to produce a rapid swelling. As the alkali then slowly diffuses out into the surrounding solution, the cellulose gel contracts, and, since the gel is fibrous in structure, consisting of strongly cohering and interlocking micelles, the contraction produces shrinkage in the direction of the fiber axis.

Other Theories of Swelling. Besides the theory of Neale, several suggestions have been put forward to explain the swelling of cellulose in alkali. All of these mechanisms may be assumed to operate to some extent in actual cases.

[27] G. F. Davidson, *J. Textile Inst.*, **27**, T112 (1936).

One of these theories also states that the swelling is a result of osmotic pressure, but that the pressure is due to dissolved cellulose molecules in the fiber. Davidson[27, 28] demonstrated that solubility, like swelling, passes through a maximum and that both of these maxima occur at approximately the same alkali concentration. In Figure 18 the solubility of cellophane at various temperatures is shown as a function of sodium hydroxide concentration, and in Figure 19 the swelling is compared with

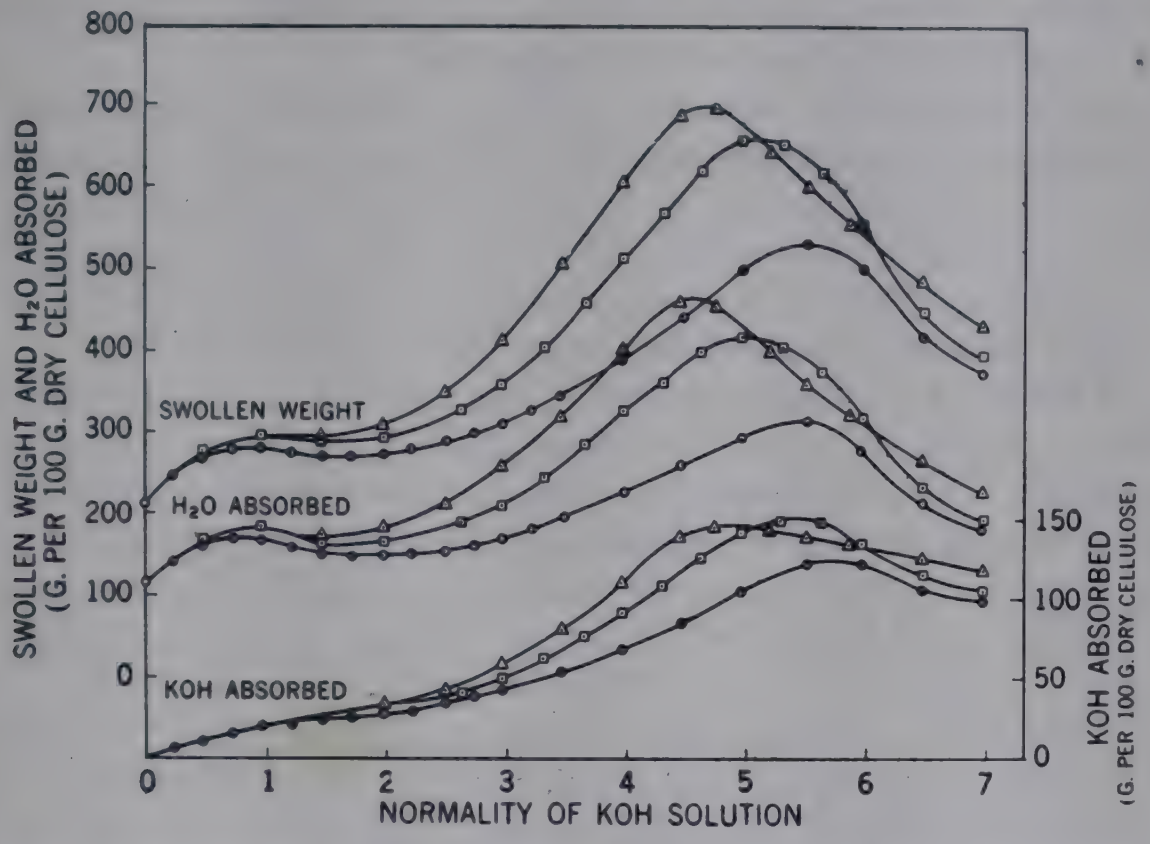

FIG. 19.—SWELLING AND SOLUBILITY OF CELLOPHANE IN KOH SOLUTIONS (DAVIDSON[27]).

⊙—At 15°C.
⊡—At 0°C., adding cellophane at 15°C.
△—At 0°C., adding cellophane at 0°C.

the solubility of the same material in potassium hydroxide. The solubility is expressed as the ratio of dissolved to undissolved material in a large excess of aqueous alkali. The fact that the solubility in sodium hydroxide is much greater than in potassium hydroxide corresponds also to the behavior observed with the swelling.

A second explanation is that the swelling is caused by hydration; that is, by the cohesive forces between the alkali cellulose compound and the water molecules. With increasing concentration of alkali hydroxide, there is an increasing competition between the free Na^+ and OH^- ions and the

[28] G. F. Davidson, *J. Textile Inst.*, **25**, T174 (1934).

alkali cellulose for the water molecules; consequently, the hydration of the alkali cellulose compound diminishes. It is interesting to note in this connection that, according to Hess and his collaborators,[29] the crystallized alkali cellulose contains water of hydration. At the lower alkali concentrations, the stable soda cellulose I contains 3 moles of water per $C_6H_{10}O_5$ compared with 1 mole of water per $C_6H_{10}O_5$ in the soda cellulose II, which is stable only at higher alkali concentrations. However, the swelling, especially that of the regenerated cellulose, is too extensive to be attributed solely to the amount of water of crystallization.

A third explanation is that the swelling is caused by the electrostatic repulsion between the cellulose particles which, on account of the ionization of the alkali cellulose, possess an excess of negative charges. At higher alkali concentrations the free ions exert a screening effect on the electrostatic repulsion. This is, of course, associated with the reduction of osmotic effect considered in the discussion of the theory of Neale.

Heat of Swelling. When cellulose is treated with an alkali solution of sufficient strength to produce swelling, heat is developed. Several investigators[30, 31] have attempted to measure the heat liberated with the object of relating the heat of reaction with the degree of swelling and compound formation. For caustic solutions up to 10 molar, the results have been in fairly good agreement for cotton cellulose and indicate that the heat of mercerization increases with the strength of the solution, but is not proportional to it. Barratt and Lewis[32] as well as Neale[18] obtained a definite deflection between 3 and 4 molar concentration indicating a sharp rise in the heat produced (Fig. 20). It will be recognized that this range of alkali concentration coincides perfectly with that shown by other methods to produce mercerization and formation of an alkali cellulose compound. It is also in this range that the x-ray structure has been observed to change markedly. Barratt and Lewis[32] further found that a less marked increase in heat evolved was obtained above 10 molar concentration of alkali, but Neale[18] did not confirm this and has stated that the heat evolved continues to rise rapidly for solutions containing up to 20 molar concentration of sodium hydroxide. Neale[18] also found that the curve representing heat evolved by regenerated cellulose on swelling was different from that found for cotton. With the regenerated cellulose, the initial steep rise in the curve was obtained in solutions of less than 2 molar con-

[29] H. Sobue, H. Kiessig, and K. Hess, *Z. physik. Chem.*, **B43**, 309 (1939).
[30] I. Okamura, *Naturwissenschaften*, **21**, 393 (1933).
[31] J. L. Morrison, W. B. Campbell, and O. Maass, *Can. J. Research*, **B18**, 168 (1940).
[32] T. Barratt and J. W. Lewis, *J. Textile Inst.*, **13**, T113 (1922).

centration as compared with 3–4 molar for cotton. This was explained by the assumption of an "accessibility" factor which was considered to be greater for the relatively unorganized structure of regenerated cellulose than for the highly organized structure in cotton.

Neale's[18] conclusions have been criticized by Bancroft[9] on the basis that "heat of reaction" may just as well be called "heat of absorption," since the

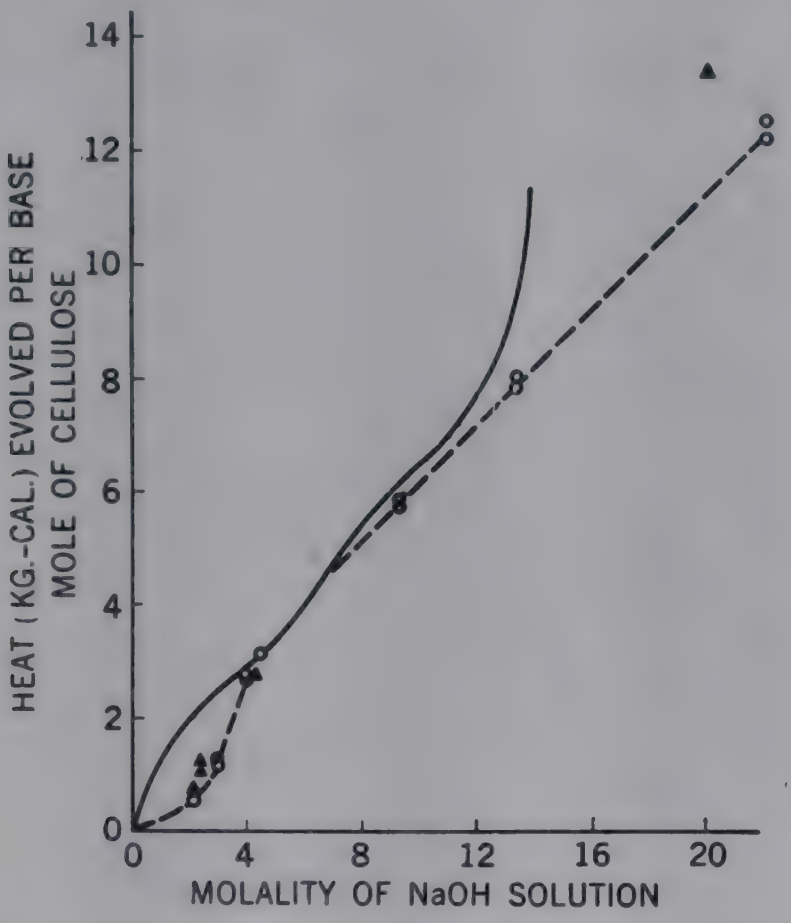

FIG. 20.—HEAT EVOLVED ON TREATING VARIOUS CELLULOSES WITH ALKALI (NEALE[18]).

——— Viscose rayon.
O —Cotton, soda-boiled.
▲ —Cotton, soda-boiled and mercerized.

thermal data obtained could be said to fit one as well as the other. It seems possible that these differences in points of view might be reconciled if it were assumed that, at the higher concentrations of alkali, the heat evolved can be due to both absorption and chemical combination while at lower concentrations, where no changes in x-ray diagram can be detected, the heat evolved is due to absorption only. As is the case elsewhere in this book, it appears proper to re-emphasize at this place the fact that the value of the forces binding NaOH to crystallized and to uncrystal-

lized cellulose chains is probably the same, but that reaction with the uncrystallized portions occurs at a lower concentration due to their greater availability. This portion of the reaction, of course, does not affect the x-ray diagram.

Effects of Added Solvent on Swelling. The addition of alcohol, alone or in combination with water, has been used by several investigators as a means of determining the nature of alkali cellulose. Both Vieweg[10] and

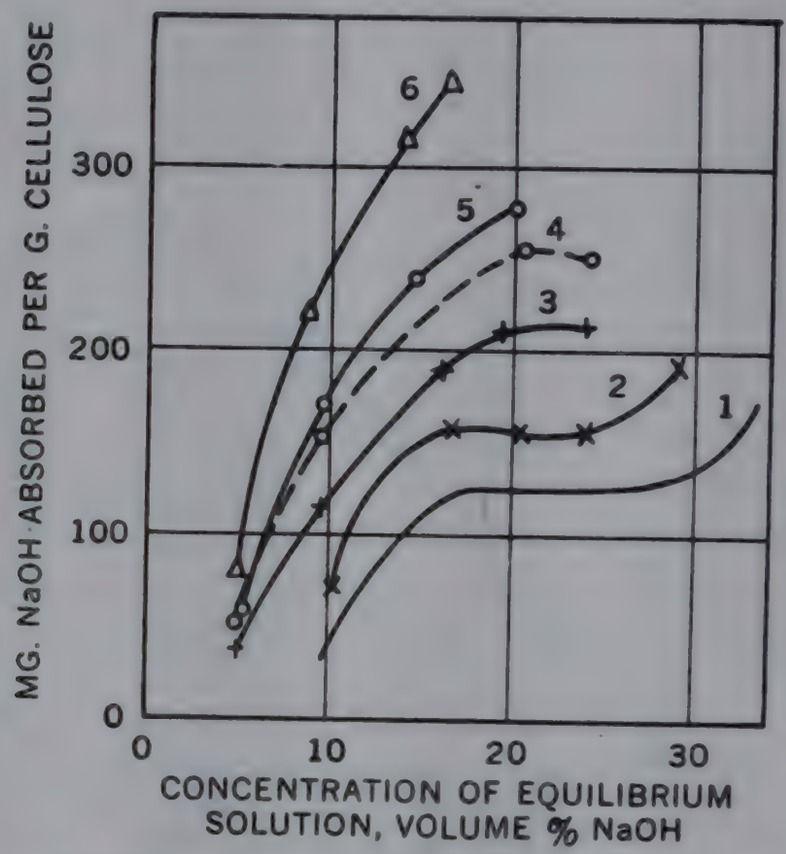

FIG. 21.—NaOH PREFERENTIALLY ABSORBED BY CELLULOSE IN THE PRESENCE OF ALCOHOL (D'ANS AND JÄGER[13]).

Curves: 1, 0% alcohol, 23°C.; 2, 10% alcohol, 23°C.; 3, 20% alcohol, 23°C.; 4, 30% alcohol, 23°C.; 5, 40% alcohol, 23°C.; 6, 20% alcohol, 2°C.

d'Ans and Jäger[13] found that for a given concentration of alkali the apparent amount of sodium hydroxide taken up by cellulose as determined by the change-in-titer method increases with increase in the amount of alcohol added. Vieweg concluded that with alcohol present no chemical combination occurred between celluloses and caustic soda. d'Ans and Jäger[13] (Fig. 21), however, obtained flat portions in the curves for 10 and 20% alcohol and showed that the absorption curves change position in relation to the alkali concentration and that the amounts of alkali absorbed at the inflection points in these curves are greater with increasing alcohol concen-

tration. Bancroft and Calkin,[9] also using the change-in-titer method, found considerably more alkali absorbed from 95% alcohol than from an aqueous solution of the same alkali concentration. Beadle and Stevens,[17] using the blotting method, noted, on the other hand, that both the total sodium hydroxide and the water absorbed decreased on addition of absolute alcohol.

It is believed that a comprehensive explanation for these divergent data might be found if it is remembered that cellulose takes up water readily, but absolute alcohol slightly, if at all.[9] Also, caustic soda is much less soluble in alcohol than in water, and, in the case of a caustic soda–alcohol–water system, the effective concentration of alkali in the water would be far greater than if no alcohol were present. In such a system the apparent increase in the alkali taken up by the cellulose would be greater by the change-in-titer method of measurement, but, because of a decrease in swelling, the over-all absorption of alkali as judged by the blotting method might actually be less. Also, if the alkali cellulose were formed first and afterward treated with alcohol, the water taken out of the cellulose by the alcohol might be expected to carry out appreciable amounts of caustic soda, though any alkali preferentially absorbed should not be affected to the same extent.

Effects of Salts on Swelling. Neutral salts, particularly sodium chloride, have been added to the cellulose–caustic soda–water system with the object of influencing swelling and the amount of alkali absorbed. The reported results again are not in complete agreement, but most investigators have found that concentrations of from 5 to 20% sodium chloride decrease swelling but increase the amount of alkali absorbed by the cellulose. Schwarzkopf,[21] d'Ans and Jäger,[13] and others have claimed that sodium chloride is itself not absorbed by cellulose in the presence of alkali, and Schwarzkopf, as we have seen, used the presence of sodium chloride as a method for determining the amount of water absorbed. Saito studied the effects produced on the amount of alkali absorbed by increasing the concentration of sodium chloride and found that, while the apparent absorption (change-in-titer method) increases gradually, the total absorption of alkali and water actually decreases slightly (Fig. 22). It is believed that these findings may be explained on the same general basis as has been used to explain the effects of alcohol on alkali cellulose.

Joyner[33] studied the effects of potassium salts and concluded that KCl has a more powerful effect than NaCl in influencing alkali absorption.

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[33] R. A. Joyner, *J. Chem. Soc.*, **121**, 2395 (1922).

Jimbo and coworkers[34] tested the effect of sodium chloride in the preparation of alkali cellulose for the viscose process. They concluded that small quantities, up to 2%, may exert a slight beneficial influence on the proper-

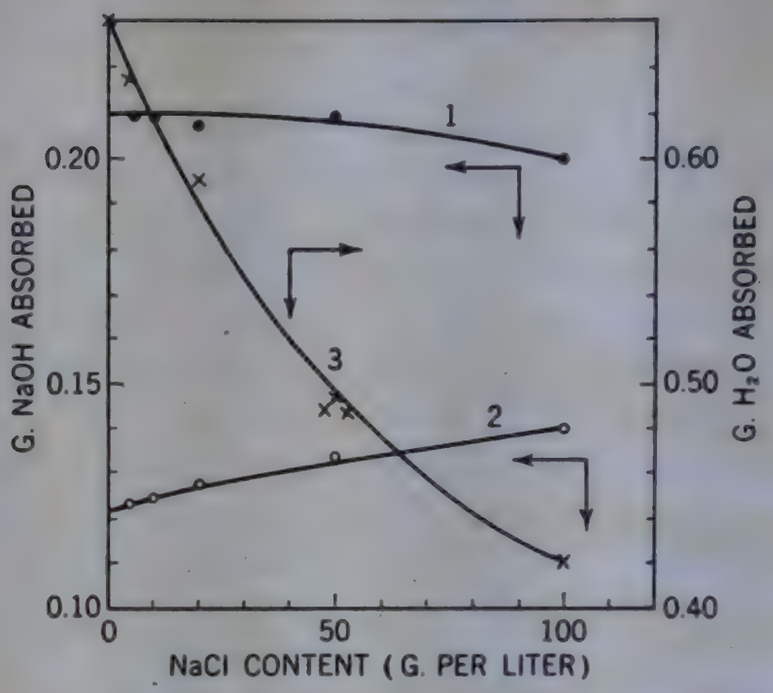

FIG. 22.—EFFECTS OF NaCl ON THE TOTAL AND PREFERENTIAL ABSORPTION OF NaOH AND TOTAL ABSORPTION OF H_2O FROM A NaOH SOLUTION (140 G. PER LITER) AT 20°C. (SAITO[6]).

Curves: 1, minimum true NaOH absorption; 2, preferential NaOH absorption 3, total absorption of water.

ties of the regenerated yarns, but that higher concentrations of salt cause difficulty in filtration, probably due to a reduction in the degree of swelling achieved during steeping.

(*d*) *Metal Hydroxides Other Than Sodium Hydroxide*

Although most of the work covering the action of alkalies on cellulose has been concerned with sodium hydroxide, some attention has also been given to the hydroxides of the other alkali metals.

Heuser and Bartunek,[35] using the hydroxides of lithium, sodium, potassium, rubidium, and cesium, found that each produces an absorption curve by the change-in-titer method which contains a break interpreted as indicating the formation of a definite compound with the cellulose (Fig. 23A). In the case of lithium and potassium hydroxides, the com-

[34] S. Jimbo, T. Takazawa, and K. Tanaka, *J. Soc. Chem. Ind., Japan*, **37**, B395 (1934).
[35] E. Heuser and R. Bartunek, *Cellulosechem.*, **6**, 19 (1925).

pounds are strictly analogous to that formed with sodium hydroxide and may therefore be represented by the general formula $(C_6H_{10}O_5)_2 \cdot MOH$ where M is the alkali metal. With rubidium and cesium hydroxides, the indicated compounds contain 3 moles of cellulose for each mole of hydroxide and would therefore be represented by $(C_6H_{10}O_5)_3 \cdot MOH$. The concentra-

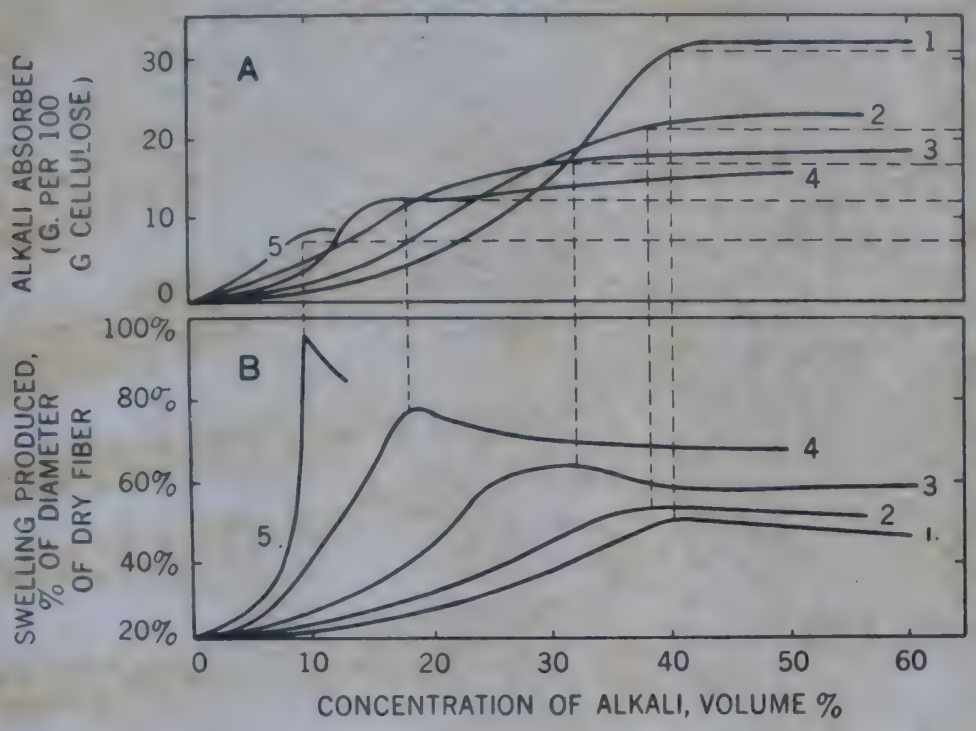

FIG. 23.—COMPARISON OF (A) THE ALKALI ABSORBED BY AND (B) THE SWELLING PRODUCED IN CELLULOSE ON TREATMENT WITH SOLUTIONS OF VARIOUS ALKALI METAL HYDROXIDES (HEUSER AND BARTUNEK[35]).

Curve	Alkali	Concentration of maximum swelling	Pseudostoichiometric ratio
1	CsOH	40%	$(C_6H_{10}O_5)_3 \cdot CsOH$
2	RbOH	38%	$(C_6H_{10}O_5)_3 \cdot RbOH$
3	KOH	32%	$(C_6H_{10}O_5)_2 \cdot KOH$
4	NaOH	18%	$(C_6H_{10}O_5)_2 \cdot NaOH$
5	LiOH	9.5%	$(C_6H_{10}O_5)_2 \cdot LiOH$

tions of alkali in solution required for the formation of these compounds follow the same order as the atomic weights of the alkali metals, which is: Li < Na < K < Rb < Cs. It is also to be noted that for the first three hydroxides the molar concentration at which the break in the absorption curve occurs is almost identical, although the per cent concentration increases.

The degree of swelling determined microscopically by observations on the cross section of the treated fiber has also been studied for the various

metal hydroxides. However, the examination of transverse sections can lead to errors on account of the so-called "dumbbell-like" swelling, which was first observed by Willows and Alexander[36] (Fig. 24). This occurs with cotton at the mercerizing concentration due to the extrusion of the cellulose from the ends of the section during the swelling process. More reliable results can be obtained by measuring the width of the whole fiber.

Heuser and Bartunek (Fig. 23B) found that, for each hydroxide, swelling of scoured cotton passes through a maximum at a concentration of alkali which corresponds closely with that producing the break in the change-in-titer curve. The degrees of swelling at the maxima for the various alkalies are in the same relative order as the degrees of hydration of the respective metal ions. The ions of lowest atomic volume are associated with the greatest number of water molecules, and maximum swelling occurs in solutions of the various hydroxides in which the MOH : H_2O ratios are the same as those corresponding to the fully hydrated ions. Temperature affects the hydration of these hydroxides so that hydration is somewhat higher at lower temperatures and lower at higher temperatures.

FIG. 24.—PHOTOGRAPH SHOWING THE "DUMBBELL-LIKE" SWELLING OF MICROSCOPIC SECTIONS OF COTTON FIBERS IN MERCERIZING SOLUTIONS (WILLOWS AND ALEXANDER[36]).

Saito[6] studied the absorption of alkali and water by cellulose from solutions of lithium, sodium, and potassium hydroxides by using the alkali-neutral salt method. The data obtained agree at least qualitatively with those found by the change-in-titer method and indicate breaks in the curves for preferentially absorbed alkali at about the same molar concentrations. Swelling at the maxima was found to decrease with increase in the molecular weight of the alkali. Saito[6] also studied effects obtained through the use of mixtures of these alkalies, taken two at a time, the results being of interest chiefly because the values found did not always lie intermediate between the values produced by either alkali alone. Mixtures of lithium and potassium hydroxides, for example, produce swelling values which pass through a maximum at a ratio of 1 : 1. Mixtures of lithium and sodium hydroxides, on the other hand, produce values showing a minimum at approximately a 1 : 1 ratio. The only mixtures behaving normally were

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[36] R. S. Willows and A. C. Alexander, *J. Textile Inst.*, **13**, T237 (1922).

those containing sodium and potassium hydroxides, for which all swelling values are intermediate between those characteristic of each alkali alone.

(e) *Effects Produced by Dilution or Concentration of Alkali Solutions*

The curve for alkali absorption determined by the change-in-titer method is not retraced exactly when a strong solution of alkali in contact with cellulose is diluted. In the case of cotton cellulose, for example,

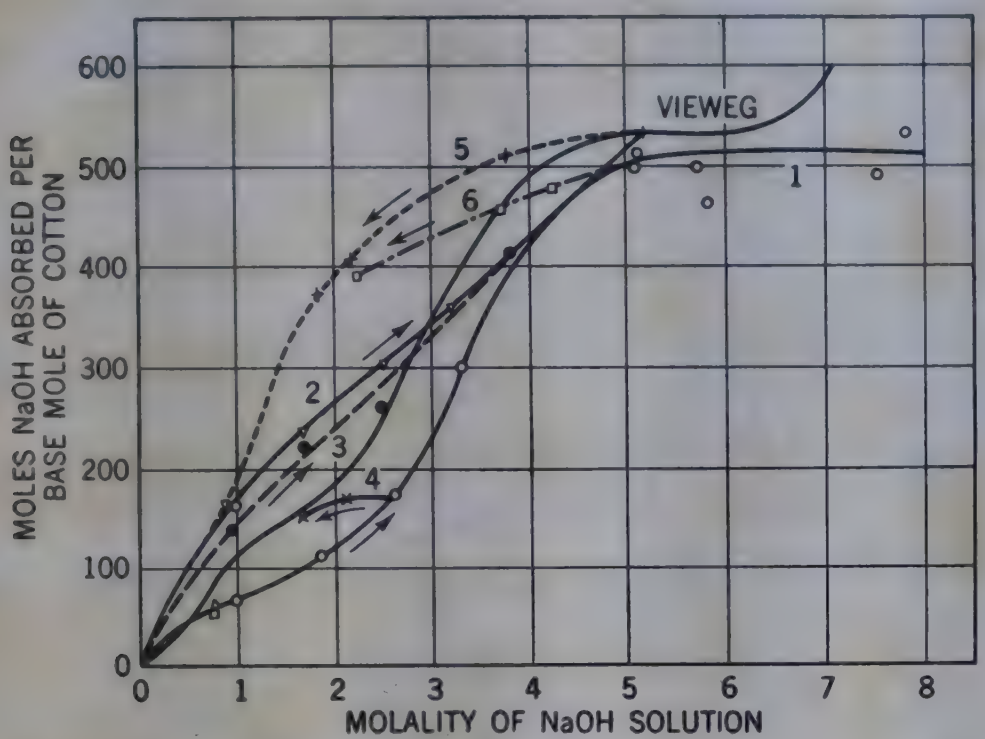


FIG. 25.—PREFERENTIAL ABSORPTION OF ALKALI OBTAINED ON DILUTION AND CONCENTRATION OF SOLUTIONS OF NaOH (BANCROFT AND CALKIN[9]).

Curves

Concentration	Dilution
1—○	4—×
2—▽	5—+
3—●	6—□

Vieweg (no points)

Bancroft and Calkin[9] found that dilution of a 5 *M* alkali solution gave values for alkali absorption which were considerably greater than those obtained either by direct treatment with solutions of equivalent concentrations or by progressively increasing the concentration of alkali in solution (Fig. 25). It has been similarly shown by Saito[6] that, with both ramie and cotton cellulose, progressively decreasing the concentration of alkali in solution produces a shift in the swelling maximum in the direction of lower alkali concentration (Fig. 26). The extent of the shift appears to be

dependent on the initial concentration of the alkali used and, within limits, increases with this initial concentration. Evidence points, therefore, to the conclusion that alkali absorption and swelling are both irreversible phenomena, although the alkali can be entirely removed if the cellulose is washed thoroughly with water.

Saito[6] also obtained data for changes in swelling when the concentration of alkali is increased stepwise. Under such conditions fibers remain greatly swollen at the higher concentrations, although normally they are not so highly swollen if the cellulose is introduced directly. This investigator also studied the effects of varying the temperature of the alkali

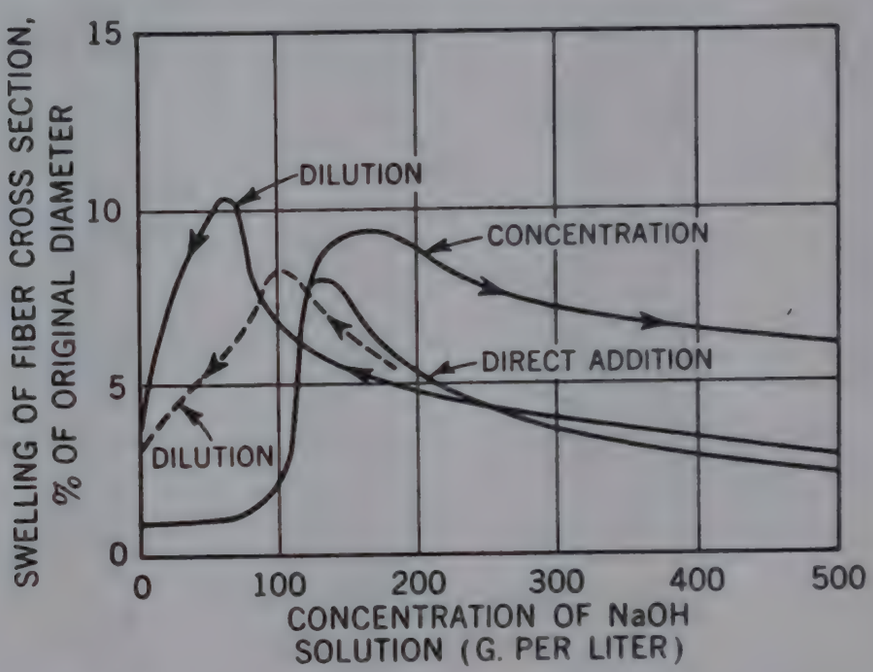


FIG. 26.—COMPARISON OF EFFECTS ON THE SWELLING OF RAMIE CELLULOSE OBTAINED BY DILUTION AND CONCENTRATION OF SOLUTIONS OF NaOH (SAITO[6]).

solution over the range 14–31°C. when using 130 g. per liter of sodium hydroxide. Comparisons were made between conditions in which the cellulose was already introduced into the alkali solution and the temperature then either increased or decreased, and conditions obtained by adding the cellulose directly to solutions at 14°, 20°, and 31°C., respectively (Fig. 27). From this graph it is apparent that, if the cellulose is initially introduced into a cold solution of alkali, the amount of alkali absorbed is not changed appreciably by increasing the temperature, although this is not true if the cellulose is introduced at a higher temperature and the solution allowed to cool. To some degree the same relationships hold for swelling, since the decrease in swelling obtained by increasing temperature

s slight in comparison with the increase in swelling obtained by decrease n temperature. These observations, in general, may be considered to onfirm the nonreversible character of the swelling process.

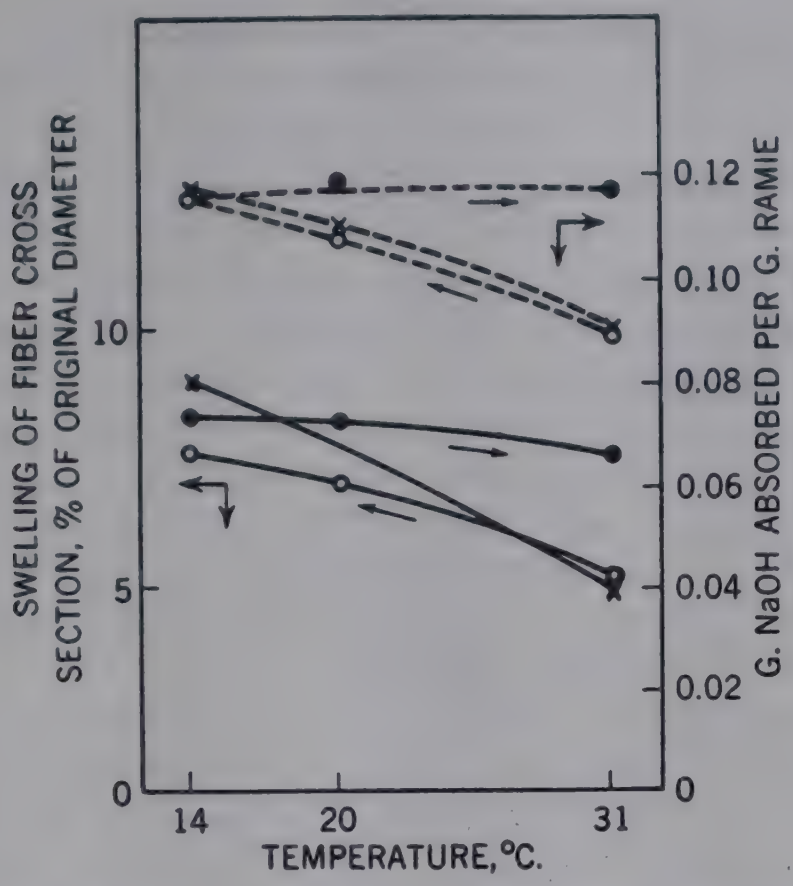


FIG. 27.—EFFECTS OF TEMPERATURE ON SWELLING AND ALKALI ABSORPTION OF RAMIE CELLULOSE IN NaOH SOLUTIONS (130 G. PER LITER) (SAITO[6]).

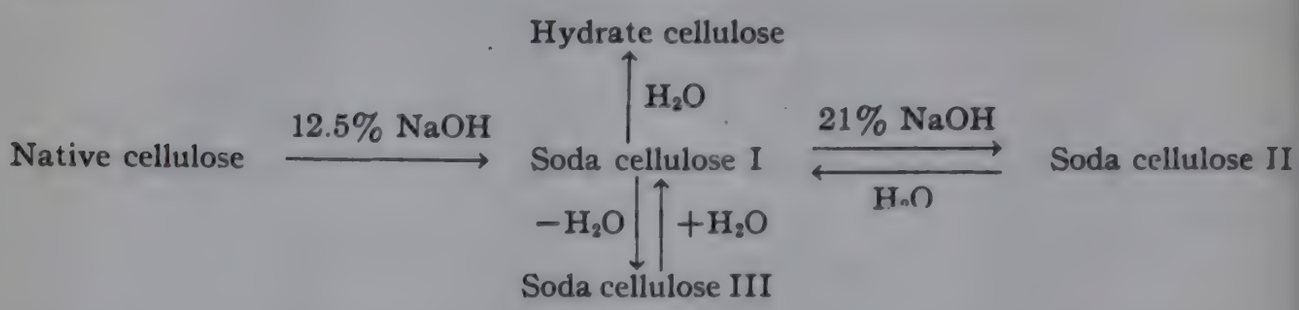
○—Decreasing temperature.
●—Increasing temperature.
×—Direct introduction of cellulose.

(*f*) *Examination of Alkali Cellulose by X-Rays*

The application of x-rays to the study of alkali cellulose has been of tremendous value in helping to clarify questions regarding the nature of the material itself and the changes which take place when cellulose is treated with alkali solutions of different concentrations. Evidence supplied by Hess and Trogus,[37] von Susich and Wolff,[38] and others indicates that certain definite changes take place in the crystalline structure of cellulose when treated with sodium hydroxide solutions. The principal

[37] K. Hess and C. Trogus, *Z. physik. Chem.*, **B4**, 321 (1929); **B11**, 381 (1930).
[38] G. von Susich and W. W. Wolff, *Z. physik. Chem.*, **B8**, 221 (1930).

relationships found by these workers may be summarized by the following scheme:



The changes in crystal structure, while strongly suggesting the formation of definite compounds, do not occur sharply but show a gradual transition over a range of several per cent alkali. This, as already noted, agrees with observations made on the alkali absorbed by cellulose from caustic soda solutions of different concentrations. Soda cellulose I as defined by x-ray studies may therefore be identified with the ordinary alkali cellulose obtained in 16–18% alkali, and soda cellulose II is probably identical with the product of mercerization as normally carried out in the stronger alkali solutions used in the treatment of textiles.

More recently Neumann[39] found that, if soda cellulose I is made from a hydrate cellulose and the concentration of alkali in solution is gradually decreased, there is formed below about 6% alkali concentration a fourth modification in crystal structure, which he termed soda cellulose IV. Following this, Schramek and Görg[40] found that, if soda cellulose I derived from hydrate cellulose is treated with caustic soda of 25–28% concentration, it may be converted temporarily into still another crystal form which was termed soda cellulose V. The latter is not stable, however, and on standing gradually reverts to soda cellulose II. If the alkali concentration in contact with soda cellulose II is then reduced, further changes occur as indicated by a gradual transition through soda cellulose I and, below 6% alkali, to soda cellulose IV. Still more recently, Sobue[41] has shown that at low temperatures where swelling is very high, two further compounds of cellulose and sodium hydroxide may exist. These have been designated as soda cellulose VI and soda cellulose Q. Sobue has summarized the interrelationships of most of the known soda cellulose compounds as revealed by x-ray methods (Fig. 28).

The importance of swelling in the formation of the various crystalline

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[39] H. Neumann, Dissertation, Dresden, 1933.

[40] W. Schramek and H. Görg, *Kolloid-Beihefte*, **42**, 302 (1935).

[41] H. Sobue, *J. Soc. Chem. Ind., Japan*, **43**, B24 (1940).

modifications of alkali cellulose detectable by x-rays is shown by the fact that if hydrate cellulose is used, the conversion to soda cellulose I takes place at a lower concentration of alkali than is the case with native cellulose. Moreover, soda cellulose I, made from hydrate cellulose, does not convert to soda cellulose II in 20–25% sodium hydroxide but only in above 28% sodium hydroxide. Observed differences in the alkali concentration ranges which give rise to a given lattice structure under conditions of increasing caustic concentration, as opposed to decreasing caustic concentration, are also most readily explained on the basis of swelling.

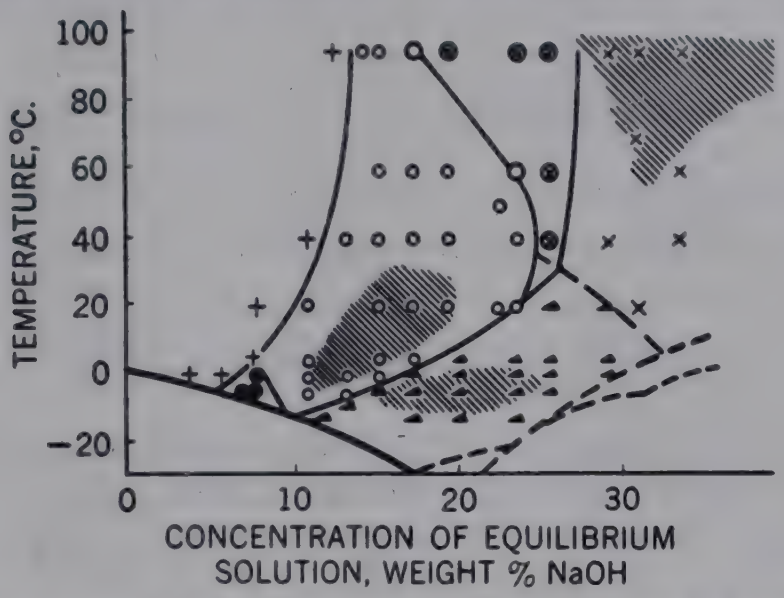

FIG. 28.—CHANGES IN THE X-RAY DIFFRACTION DIAGRAMS OF ALKALI CELLULOSE DUE TO TEMPERATURE AND CONCENTRATION OF ALKALI IN SOLUTION (SOBUE[41]).

⊗—Soda Cellulose III. +—Native Cellulose.
○—Soda Cellulose I. ×—Soda Cellulose II.
●—Soda Cellulose Q. ▲—Soda Cellulose V.

Further evidence of the importance of swelling on change in crystal structure is the fact that soda cellulose I is not obtained in water-free solutions of sodium hydroxide-methanol which are known to be poor swelling agents for cellulose. Tension, which is also known to affect swelling, has been found to affect changes in the x-ray diffraction diagram. On the basis of this relationship, Hess and Trogus[37] were able to show that ramie under tension could be treated with 30–35% caustic soda and subsequently washed without any evidence of a hydrate being formed. It may be inferred, therefore, that swelling is absolutely necessary in order for the alkali to penetrate into the cellulose lattice. Also, the degree of preswelling definitely helps to determine the amount of alkali absorbed and the crystal structure formed when cellulose is treated in an alkali solution of a given concentration.

(g) *Chemical Reactions of Alkali Cellulose*

From a purely chemical standpoint, the principal properties of alkali cellulose are consistent with those to be expected for a metal alcoholate derived from a polymeric carbohydrate containing reactive hydroxyl groups. As a typical alcoholate, alkali cellulose reacts with halogen compounds to form ethers:

$$R_{cell}—ONa + RCl \longrightarrow R_{cell}—OR + NaCl$$

Alkali cellulose also reacts with acid anhydrides and acid chlorides to form esters:

$$R_{cell}—ONa + ROCl \longrightarrow R_{cell}—OOR + NaCl$$

Undoubtedly, the most important ester prepared from alkali cellulose is sodium cellulose xanthate obtained through reaction with carbon disulfide, thus:

$$R_{cell}—ONa + SCS \longrightarrow R_{cell}—OCSS{\cdot}Na$$

Each of these reactions is important in itself, both chemically and from the commercial point of view, but they will not be discussed in detail here as they are described thoroughly in Sections E, C, and F, respectively, of this chapter.

Aging of Alkali Cellulose. The reaction of alkali cellulose with oxygen or oxygen-producing compounds is of a somewhat different character from its other reactions in that the most important effect produced is a degradation of the cellulose brought about by combination with oxygen and subsequent splitting of the chain molecules. Cross, Bevan, and Beadle,[4] the discoverers of the viscose process, recognized that if pressed alkail cellulose is allowed to stand for any appreciable length of time, changes take place resulting in a decrease in the solution viscosity of the cellulose. This process, known as "aging," has been the subject of much study from both the practical and theoretical points of view.

Although certain early workers ascribed the effects accompanying aging solely to the action of the alkali, most of the evidence has indicated that oxygen of the air in the presence of the alkali is an essential condition of the aging process. As early as 1906, Margosches,[42] and later Ost[43]

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[42] B. M. Margosches, *Die Viskose.* 2nd ed., Verlag der *Z. ges. Textil-Ind.* (*Klepzig's*), Leipzig, 1906.

[43] H. Ost, F. Westhoff, and L. Gessner, *Ann.*, **382**, 340 (1911).

(1911), recognized oxidation as having an important part in the aging process without, however, investigating in detail the mechanism involved.

In addition to the decrease in viscosity, other major changes which cellulose undergoes during aging are an increase in the alkali solubility, a slight increase in reducing power, and the formation of carboxylic acid groups. The extent to which these changes occur depends primarily upon the oxygen concentration, the temperature, and the duration of the aging, but is also affected by the origin and previous history of the cellulose, the concentration of the steeping solution, the press ratio, and the presence or absence of certain oxidation catalysts or inhibitors.

In the past, some investigators have minimized the influence of oxygen and assumed that aging is mainly a continuation of physical changes initiated by swelling of the cellulose in a strong solution of caustic soda. It has been postulated that swelling results in a breakdown of secondary valence forces holding the micelles or cellulose chains together. More recently, however, it has been shown[44] that the changes undergone during aging are very different in character from those occurring during the swelling of mercerization. For example, during mercerization the cellulose swells and, because of the increase in internal surface thus created, becomes more reactive toward all types of chemical and physical attack, but undergoes almost no change in degree of polymerization. During aging, on the other hand, chemical activity, as measured by rate of hydrolysis or xanthate formation, does not increase, although the solution viscosity is greatly affected.

New light on the mechanism of the aging process was obtained when Waentig[45] showed that no aging takes place if air is excluded by covering the cellulose with liquid caustic soda. After this observation, various studies were made with the object of determining more exactly the rate of oxygen absorption and the role played by oxygen in the aging process. The first investigators to measure carefully the amount of oxygen absorbed were Weltzien and zum Tobel,[46] who found that alkali cellulose prepared from an 18% solution of caustic soda reached a maximum absorption of 140 cc. of oxygen per g. of cellulose after exposure for 360 hrs. at 60°C. These investigators also found that the absorption of oxygen passes through

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[44] O. Faust and P. Karrer, *Helv. Chim. Acta*, **12**, 414 (1929); S. M. Lipatov and N. A. Krotova, *Iskusstvennoe Volokno*, **7**, 1112 (1930); S. M. Lipatov and E. Ya. Vinetskaya, *Iskusstvennoe Volokno*, **5**, 2; **6**, 2 (1931); Z. A. Rogovin and M. Schlachover, *Iskusstvennoe Volokno*, **5**, 3 (1933).

[45] P. Waentig, *Kolloid-Z.*, **41**, 152 (1927).

[46] W. Weltzien and G. zum Tobel, *Ber.*, **60B**, 2024 (1927).

a maximum by steeping in solutions of about 25% caustic soda. The conditions used in these experiments were, of course, extreme but indicate clearly that cellulose can be oxidized to a considerable extent.

The acidic products of oxidation found by Weltzien and zum Tobel included considerable amounts of carbon dioxide. These products neutralized much of the alkali originally present and caused the oxygen consumption to slow down toward the end of the experiment. This indicated that the concentration of alkali present is also of importance in the aging process. The same investigators studied the aging of alkali cellulose in an atmosphere of nitrogen or hydrogen and covered with an organic liquid which prevented contact with the atmosphere. Under these conditions, oxidation was greatly retarded but aging was not eliminated completely.

More recently, Staudinger and Jurisch[47] have shown that in a high vacuum no aging of alkali cellulose occurs even after standing for 8 days at 20°C. and that aging is very slight after a similar treatment at 100°C. Staudinger followed the changes occurring during aging by measuring the viscosity of cellulose solutions in low-concentration cuprammonium hydroxide solvent. The conclusion was drawn that the changes in alkali cellulose produced by aging are due entirely to degradation of the cellulose molecule by atmospheric oxygen. It was also shown that the oxygen consumed during normal aging increases with the amount present, but aging will proceed with very small concentrations. For a given concentration, the amount of oxygen consumed is linear with time and is quite small for ordinary alkali cellulose. The curve for aging time versus viscosity is a hyperbola and the logarithm of the viscosity will form a straight line when plotted against the logarithm of the time.[48]

The mechanism of the chemical processes by which the cellulose chains are ruptured during aging is still not fully known. The principal reasons for this are, of course, the difficulties involved in isolating and identifying intermediate products of the reaction. Plausible hypotheses which can be advanced at this time to explain aging are based on "chain" reactions in which the first stage is an addition of oxygen at some point, not yet definitely determined, in the pyranose ring. An unstable structure results, the ring opens, and fission occurs, probably at the 1,4- acetal linkages but possibly at some other point. The first attack might be on carbon atom 1, but might equally well occur on the hydroxyl groups attached to carbon atoms 2 and 3. After splitting of the chain, rearrangement probably follows, resulting in the formation of a carboxylic acid group on the end of

[47] H. Staudinger and I. Jurisch, *Zellstoff u. Papier*, **18**, 690 (1938).

[48] O. Eisenhut, *J. prakt. Chem.*, **157**, 338 (1941).

t least one fragment of the original cellulose chain. Aldehyde groups re probably formed at intermediate stages in the process but, inasmuch s the increase in copper number observed during aging is small, they must ndergo further rapid oxidation to more stable carboxyl groups.

ractical Applications of the Aging Reaction. From the technical standoint, it is more important to appreciate the influences of certain chemal and physical factors affecting the aging process than to understand ully the chemical mechanism of the process. Aging is principally of nterest as a method of controlling solution viscosity, and changes in iscosity are the criteria for estimating the degree of aging produced. he changes in viscosity may be determined conveniently by a cupramonium viscosity measurement of the regenerated celluloses or by xanthaion of the aged alkali cellulose and measurement of the viscosity of the esulting viscose. The effect of time on aging and viscosity has already een mentioned and may conveniently be followed by means of a log–log urve. Temperature, as might be expected, has a marked effect on aging, nd the rate of change in viscosity at 65°C., for example, is approximately wenty times that at 25°C. (Fig. 29).

The type of cellulose affects the rate of aging. It appears probable that he major reason is that differences in swelling characteristics of the differnt types of cellulose affect the amount of surface available for reaction vith oxygen. The presence in cellulose of certain metallic impurities is lso known to be important because they can act as catalysts for the xidation reaction. In any case, it is usually necessary in the viscose rocess to determine the rate of aging for each new type of cellulose used.

The concentration of alkali in the steeping liquor also affects aging, vhich, as has been shown, increases with increase in the concentration of austic soda up to about 25% NaOH. However, under commercial condiions in the viscose process, this variable is not generally encountered, ince the solution used almost always contains between 17 and 18% NaOH. he ratio of the weight of the pressed alkali cellulose to the weight of the riginal cellulose, commonly known as the press ratio, has a slight effect n the rate of aging. As the press ratio is decreased, the time required to each a given viscosity increases, but it is not known whether this effect s due to the decrease in the total alkali contained in the pressed alkali ellulose, or to the fact that the alkali cellulose is generally shredded less fficiently at low press ratios.

Before concluding this discussion of aging, mention should be made of he effects produced by certain metal ions which may be present, either in he pulp or in the steeping caustic, and which exert a catalytic effect on

the oxidation process. Iron has long been recognized as a factor affecting the rate of aging, and Hooker and his coworkers[49] give data on the quantitative relation between iron content in the steeping caustic and the rate

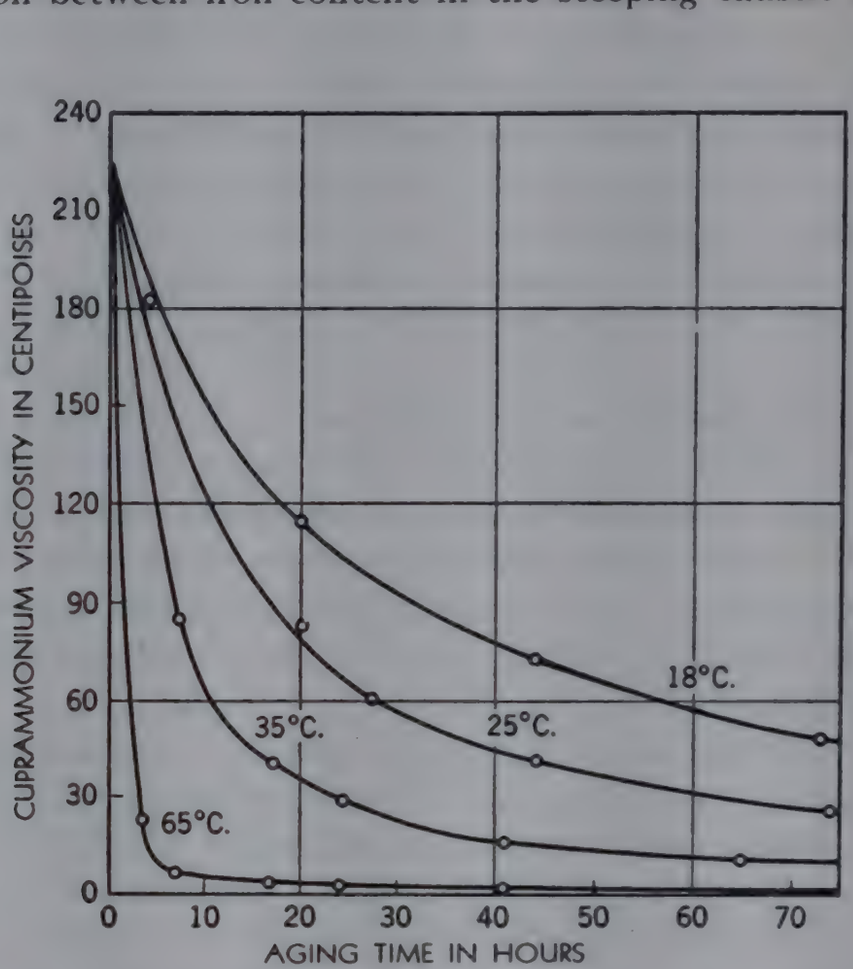

FIG. 29.—EFFECT OF TEMPERATURE ON RATE OF AGING OF ALKALI CELLULOSE (COURTESY OF CONAWAY).

of viscosity reduction during aging (Fig. 30). The effect of manganese is almost ten times that of iron,[50] and nickel has also been shown to catalyze aging, while copper inhibits the reaction slightly. Cowling[51] found that manganese apparently increases the efficiency of the oxidation reaction and produces a greater loss in viscosity for a given amount of oxygen than can be obtained without manganese present. Other substances known to accelerate the rate of aging are sodium sulfide and certain materials of organic origin such as polyhydric alcohols. Phenolic-type compounds, on the other hand, act as antioxidants and are known to retard the aging

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[49] A. H. Hooker, B. H. Ritter, and S. F. N. MacLaren, U. S. Patent 2,079,120 (May 4, 1937).

[50] F. E. Bartell and H. Cowling, *Ind. Eng. Chem.*, **34**, 607 (1942).

[51] H. Cowling, Dissertation, Michigan, 1939.

rocess. Finally, various active oxidizing agents such as peroxides and ypochlorites may be added to the steeping caustic to accelerate the aging rocess.

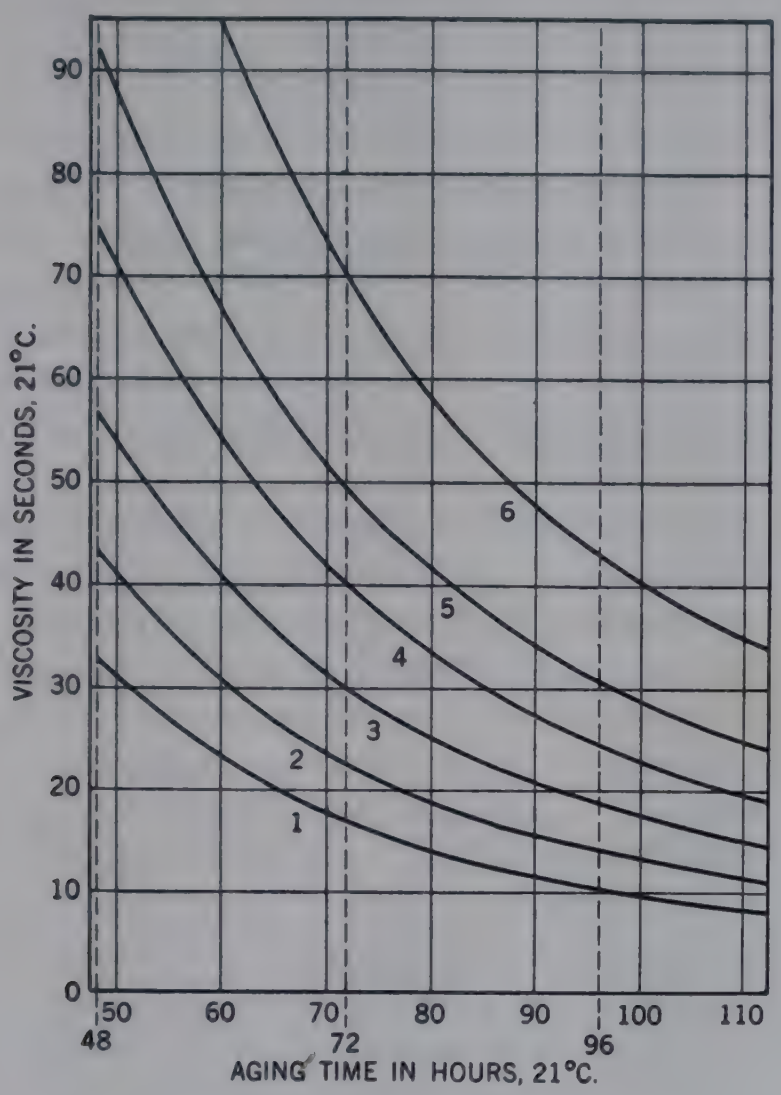


FIG. 30.—EFFECT OF IRON IN STEEPING CAUSTIC ON RATE OF AGING OF ALKALI CELLULOSE (HOOKER, RITTER, AND MACLAREN[49]).

Curve	1	2	3	4	5	6
Parts Fe per million parts NaOH	128	64	32	16	9.6	4

Industrial Preparation of Alkali Cellulose. Production of alkali cellulose in the viscose rayon industry is normally accomplished by steeping the cellulose in the form of sheets set on edge in a large horizontal tank equipped with a powerful hydraulic ram movable lengthwise through the tank. Both the steeping and pressing out of the excess caustic soda solution are accomplished in the one piece of equipment. The time of steeping normally is from 30 minutes to one hour, after which the excess liquor is drained off,

the ram started, and the sheets of alkali cellulose pressed to the desired degree, usually to about three times the original weight of the cellulose.

After the alkali cellulose is formed, the next step in the process is to shred or disintegrate the pressed sheets so as to produce a material having the large surface essential for uniform reaction with carbon disulfide. Shredding is normally done in large disintegrators of the so-called Werner-Pfleiderer type equipped with heavy rotating arms operating against a serrated saddle. The shredders are jacketed for circulation of hot or cold water in order to control temperature, because aging is already under way at this stage as a result of removal of the excess caustic liquor by pressing. After the shredding operation, the aging process proper is completed by storing the alkali cellulose crumbs in metal or fiber containers under conditions of constant temperature. For a fuller discussion of this process, see Section F of this chapter.

Except for a general increase in the size of the equipment units used in the foregoing operations, few fundamental changes have been introduced in the methods of making alkali cellulose since the early days of the industry. Proposals have been made[52] to modify the process to make it conform more nearly to modern continuous methods of manufacture, but progress in this direction is slow. However, it has been reported that in Europe alkali cellulose is produced continuously for use in some of the newer plants making staple fiber. One such method[53] starts with the pulp in the form of large rolls in place of sheets, and the continuous web of cellulose is led through a long steeping tank at the end of which the excess liquor is squeezed out between closely set rolls having a uniform clearance. The pressed alkali cellulose is then immediately passed in festoons through a large enclosed chamber where the aging is accomplished quickly at a somewhat higher temperature than that used in the standard process. In the final step of the process, the web of alkali cellulose is broken up by putting it through a shredding machine consisting essentially of a barbed roller which tears the pulp apart uniformly. An alternative procedure is to shred the alkali cellulose before aging and to accomplish aging either by passing the shredded material in the form of a loose blanket through an oven, or by passing it slowly through a cylinder of large diameter which rotates on a fixed axis somewhat after the manner of a cement kiln. Alkali cellulose can also be produced by a slurry steeping process using either water-wet pulp taken directly from the pulp mill or dried sheets which are beaten up in a tank with a mercerizing solution of

[52] A. Faberj, *Seta Artificiale*, **4**, 3 (1932); O. Faust, *Z. Ver. deut. Ing.*, **80**, 981 (1936).

[53] F. Steimmig, German Patent 604,015 (Oct. 17, 1934).

austic soda. This method offers the possible advantage that it insures uniform reaction between the cellulose and caustic soda. Removal of the excess alkali may be accomplished conveniently by centrifuging, by passing the material through spaced rollers, or by formation of a web such as can be done on a paper machine. The pressed alkali cellulose may then be disintegrated by any of the methods discussed above.

2. Metal Alcoholates of Cellulose

(a) *Preparation and Properties*

The discovery in 1931 by Scherer and Hussey[54] of a process for preparing the trisodium alcoholate of cellulose by treating cotton linters with metallic sodium in liquid ammonia created considerable interest and speculation in cellulose chemistry, since it opened a new frontier in the investigation of the metal derivatives of cellulose. Kraus and White[55] had shown previously that when simple monohydric alcohols are treated with metallic sodium in liquid ammonia, sodium alcoholates are formed with the liberation of an atom of hydrogen for each atom of sodium consumed, according to the following reaction:

$$ROH + Na \longrightarrow RONa + {}^1/_2H_2$$

The formation of the alcoholates of the simple alcohols involves reaction in a homogeneous system, whereas the comparable reaction of fibrous cellulose materials with sodium in liquid ammonia involves a heterogeneous reaction system. A quantitative study of the formation of the sodium alcoholate of cellulose by Scherer and his students showed that a mole of dry cellulose reacts with a maximum of three atoms of sodium, although any degree of substitution less than three can be obtained with the liberation of an equivalent amount of hydrogen. Schorigin and Makarowa-Zemljanskaja[56] substantiated Scherer's results as to the formation of a true metal alcoholate of cellulose and as to the fact that only three atoms of sodium react with each glucose unit in the cellulose structure. Schmid and his coworkers,[57, 58] as well as Muskat,[59] prepared the metal alcoholates of simple carbohydrates such as glucose, inulin, and water-soluble starches. According to these investigators, potassium and lithium form alcoholates

[54] P. C. Scherer, Jr., and R. E. Hussey, *J. Am. Chem. Soc.*, **53**, 2344 (1931).
[55] C. A. Kraus and G. F. White, *J. Am. Chem. Soc.*, **45**, 768 (1923).
[56] P. Schorigin and N. N. Makarowa-Zemljanskaja, *Ber.*, **69B**, 1713 (1936).
[57] L. Schmid and B. Becker, *Ber.*, **58B**, 1966 (1925).
[58] L. Schmid, A. Waschkaw, and E. Ludwig, *Monatsh.*, **49**, 107 (1928).
[59] I. E. Muskat, *J. Am. Chem. Soc.*, **56**, 693, 2449 (1934).

with the carbohydrates in the same manner as sodium, but attempts to obtain an alcoholate with calcium were not successful.

The trisodium alcoholate of cellulose is prepared by dissolving 3 moles of sodium in an excess of liquid ammonia at temperatures of −33 to −50°C. and adding 1 mole of carefully dried cellulose to the blue solution. The reaction is allowed to proceed in the absence of moisture from the air until the characteristic blue color of the solution disappears. In the absence of catalysts, this reaction requires several hours in which the rate of hydrogen evolution diminishes slowly as the reaction proceeds. This decrease in reaction rate varies with different types of cellulose and is probably determined by the accessibility of the hydroxyl groups in the amorphous and crystalline portions of the cellulose structure rather than by a specificity in the reactivity of the three hydroxyl groups in the cellulose structure. Scherer and Gotsch[60] have shown that the reaction time can be decreased from several hours to a few minutes by the addition of 1% of a sodium halide to the liquid ammonia system. Furthermore, the presence of a small amount of metallic iron accelerates the rate of solution of metallic sodium in liquid ammonia. The alcoholates of cellulose can probably be prepared from sodamide in liquid ammonia, since Miller and Siehrs[61] were successful in forming the potassium alcoholates of the simple carbohydrates by this method. Since sodamide is soluble in liquid ammonia to the extent of only 0.607 g. per 100 cc. at −34°C., this procedure for preparing the sodium alcoholates would probably be extremely slow.

Although attempts to prepare sodium and potassium alcoholates of cellulose by an alcohol interchange with the simple alcoholates such as sodium methylate have been unsuccessful, Harris and Purves[62] have shown that the thallium alcoholate of cellulose can be prepared by treating dry cellulose with thallous ethylate in a solution of diethyl ether or benzene. It is not possible to prepare the trithallium alcoholate of cellulose by this method, as reaction does not proceed to completion. The large thallium atoms cannot enter the crystalline or micellar portion of the cellulose structure so that only the surface hydroxyl groups are available for reaction. This steric factor enabled these workers to develop a new and ingenious method for determining the area of the internal surface or the number of available surface hydroxyl groups present in a cellulose structure by treating the thallium alcoholate of cellulose with methyl iodide and determining the extent of methylation. The internal surfaces of carefully

[60] P. C. Scherer and L. P. Gotsch, *Bull. Virginia Polytech. Inst.*, **32**, No. 11 (1939).
[61] C. O. Miller and A. E. Siehrs, *Proc. Soc. Exptl. Biol. Med.*, 29, 535 (1931).
[62] C. A. Harris and C. B. Purves, *Paper Trade J.*, **110**, 29 (Feb. 8, 1940).

urified ramie and of the corresponding mercerized fibers as determined by his method are 3.7×10^4 and 2.9×10^6 cm.^{2} per g., respectively.

The trisodium alcoholates of chemical celluloses, such as cotton linters nd wood pulp, resemble the original fibrous cellulose in physical form. 'hese metal alcoholates are, however, unstable to moisture, oxygen, and ght. When the trisodium alcoholate is exposed to atmospheric conditions, discolors rapidly with the evolution of heat accompanied by a profound egradation of the cellulose as determined by cuprammonium viscosity neasurements. In view of the extreme reactivity of these metal derivaives of cellulose, it is necessary to carry out reactions with these materials nder carefully controlled conditions.

(*b*) *Reactions of Metal Alcoholates of Cellulose*

In view of the chemical reactivity of the alcoholates of the simple lcohols in condensation reactions, it might be expected that the trisodium lcoholate of cellulose would be an ideal intermediate for the preparation f trisubstituted derivatives of cellulose, but this, in general, has not proved o be true. Miller and Siehrs[63] prepared the organic esters of cellulose y treating trisodium cellulosate with acid chlorides and anhydrides in the resence of hydrocarbon diluents. Likewise, Peterson and Barry[64] repared various cellulose ethers by treating the metal alcoholate of cellulose with alkyl halides in the presence of hydrocarbon diluents. The esulting cellulose derivatives did not appear so attractive in physical roperties as the corresponding derivatives prepared by simpler and less xpensive procedures.

Schorigin and Makarowa-Zemljanskaja[56] concluded from a study of the anthation of the sodium alcoholate of cellulose that alkali cellulose has he structure of an alcoholate. On the other hand, Scherer and Gotsch[60] howed, however, that the reaction of carbon disulfide with the trisodium lcoholate of cellulose is catalyzed by the presence of water and sodium itrate. These workers report the preparation of the trisodium xanthate of ellulose by adding 2.65% of water based on the carbon disulfide to the eaction mixture which, on the basis of their reported experiments, was ufficient water to form an 11% alkali solution with the sodium present. Since the presence of limited amounts of water seems to increase the re-

[63] C. O. Miller and A. E. Siehrs (to North American Rayon Corp.), U. S. Patent 2,181,906 (Dec. 5, 1939).

[64] F. C. Peterson and A. J. Barry (to Dow Chemical Co.), U. S. Patent 2,157,083 (May 2, 1939).

activity of the metal alcoholates of cellulose and since these compounds are known to be hydrolyzed readily by water, the conclusion is reached that, if alkali cellulose reacts as an alcoholate, the excess molecular sodium hydroxide present is extremely desirable and beneficial in the reaction system.

3. Cuprammonium-Cellulose Complexes

Schweizer[65] observed in 1857 that ammoniacal solutions of copper hydroxide dissolve certain plant and animal fibers such as cotton, linen, and silk. This important discovery is the basis of the cuprammonium or Bemberg rayon industry as well as of the viscosity determination employed in characterizing the celluloses used in the chemical and textile industries. Although many solvents for cellulose have been investigated by various workers since Schweizer's discovery, cuprammonium solutions are still the best solvents for all types of cellulose.

(*a*) *Preparation and Properties of Cuprammonium Solutions*

The compound formed when copper hydroxide is dissolved in aqueous ammonia solutions has the formula $Cu(NH_3)_4(OH)_2$, and the blue ammoniacal solutions of this compound are known as cuprammonium hydroxide solutions or simply as cuprammonium solutions. These solutions can be prepared by two general methods. In the first method, which was employed by Schweizer, a cupric salt such as copper sulfate is dissolved in an aqueous solution of ammonium chloride. Sufficient aqueous sodium hydroxide is added to the solution to precipitate all of the copper. The blue precipitate is washed thoroughly with water and dissolved in the cold in an aqueous ammonia solution. In the second method, clean metallic copper, in the form of fine pieces such as plates, turnings, or wire, is placed in a vertical tower and covered with an aqueous ammonia solution. Air is bubbled through the solution in the tower until the desired concentration of copper in the solution is obtained. The cuprammonium solution employed by the British investigators contains approximately 15 g. of copper and 240 g. of ammonia per liter, whereas the solution recommended by the American Chemical Society[66] contains 31 g. of copper and 165 g. of ammonia per liter. Many investigators add to this solution 1–10 g. of sucrose per liter as a stabilizing agent.

Cuprammonium solution is a strong reducing agent and, in addition, is

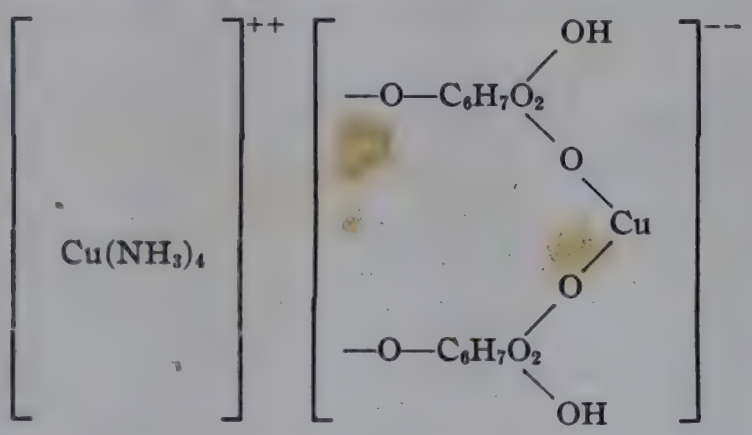
[65] E. Schweizer, *J. prakt. Chem.*, **72**, 109 (1857).

[66] E. K. Carver and Committee, *Ind. Eng. Chem., Anal. Ed.*, **1**, 49 (1929).

ecomposed by light and by standing at room temperature for a period of everal days. Due to this instability, it is necessary to use relatively fresh olutions as well as extreme precautions to protect the cellulose solutions rom oxygen and as much as possible from light. The stability of cu-rammonium solutions is increased by the solution of cellulose in this re-gent. When it is necessary to store cuprammonium for some time, it hould be placed in a dark container, blanketed with nitrogen or other nert gas, and kept at a temperature of 0–5°C. Under these conditions he solution is relatively stable for several weeks.

(*b*) *Composition of Cuprammonium-Cellulose Complexes*

Traube[67] was one of the first investigators to study the composition of uprammonium-cellulose complexes. He concluded that a compound was ormed in which part of the copper is bound in the cation and part in the nion. His formula can be represented as follows:



According to this formula the ratio of copper to cellulose in the complex is :1 although the copper is present in two different forms. Subsequent nvestigators have pointed out the limitations of Traube's formula, but to late no other proposed structure has met with unified approval.

Hess and Messmer[68] also concluded from optical rotation studies on uprammonium-cellulose solutions that the copper is combined chemically vith the cellulose but believed the compound could best be represented as salt with the structure $(C_6H_7O_5Cu)_2 \cdot (Cu(NH_3)_4)$. Bauer[69] analyzed Hess's data from a different viewpoint and obtained typical absorption curves. He pointed out that cuprammonium solutions are colloidal and concluded that the solution of cellulose in this solvent is due only to a physical peptizing action.

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[67] W. Traube, *Ber.*, **54B**, 3220 (1921); **55B**, 1899 (1922); **56B**, 268 (1923).
[68] K. Hess and E. Messmer, *Kolloid-Z.*, **36**, 260 (1925).
[69] E. Bauer, *Kolloid-Z.*, **36**, 257 (1925).

Neale[70] advanced the theory that the cuprammonium-cellulose complexes are colloidal electrolytes similar to soap, in which the strong cuprammonium base forms with cellulose, which is a weak acid, a soluble basic salt of which the cation is crystalloidal and the anion is colloidal. Neale represented the reaction involved in the solution of cellulose in cuprammonium as follows:

$$(C_6H_{10}O_5)_n + n Cu(NH_3)_4(OH)_2 \longrightarrow$$

$$[Cu(NH_3)_4]_n^{++} + [(C_6H_9O_5)]_n^{-} + [OH]^{-} + H_2O$$

This formula differs from Traube's in that all of the copper is bound in the cation. The ratio of copper to cellulose, however, is 1:1, and Neale confirmed this ratio by analyzing the precipitated and purified cuprammonium-cellulose complex. Lieser[71] has proposed still another formula which can be considered as a modification of Traube's and Neale's proposals in which 1.5 moles of copper are combined with each cellulose or anhydroglucose unit.

One of the most interesting investigations in this field was carried out by Jolley[72] in which cuprammonium solutions containing insufficient copper to effect complete solution of the cellulose fibers were studied. Under these conditions it was possible to determine the concentration of copper at equilibrium in both the solid and dissolved phases. With this technique it was possible to show that the equilibrium concentration of copper in the cellulose solution is appreciably lower than in the original solvent due to preferential absorption of the copper by the undissolved cellulose. In cuprammonium solutions of partially dissolved cotton fibers containing 200 g. of ammonia per liter, the molar ratio of copper to cellulose in the solid phase increases from 0.4 to 0.6 mole and in the dissolved phase from 0.55 to 0.75 mole as the percentage of dissolved fibers increases from 10 to 50%. Jolley also showed that the addition of small amounts of sucrose to cuprammonium solutions as a stabilizing agent decreases the solvent action of the solutions. In view of the fact that the highest concentration of copper employed in Jolley's tests was only 5 g. per liter and the dissolved phase contained 0.75 mole of copper per mole of cellulose, it is certainly reasonable that in regular solutions which contain from 15 to 31 g. of copper per liter, the ratio of copper to cellulose in the complex would increase to unity as proposed by Traube and other in-

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[70] S. M. Neale, *J. Textile Inst.*, **16**, T363 (1925).

[71] T. Lieser, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 272 (1938).

[72] L. J. Jolley, *J. Textile Inst.*, **30**, T4 (1939).

vestigators. Stamm[73] and Kraemer,[74] in determining the molecular weight of cellulose by the ultracentrifuge method, assumed that, in the cuprammonium-cellulose complex, 1 mole of copper is combined with each mole of cellulose.

The difficulties in obtaining analytical information on the cuprammonium-cellulose complex are due to the high vapor pressure of ammonia and the great excess of ammonia that is present. According to the Traube formula, ammonia should be liberated from the copper-ammonium hydroxide compound by reaction with cellulose. Attempts by various workers such as Berl and Innes[75] to determine if the vapor pressure of the ammonia increases when cellulose is dissolved in cuprammonium solution have not been entirely successful. One method of eliminating this objection is to replace the ammonia with a higher boiling diamine such as ethylenediamine. In fact a considerable portion of the structure work on cuprammonium complexes has been done with the copper hydroxide-ethylenediamine complex, which has the formula $Cu(NH_2CH_2CH_2NH_2)_2(OH)_2$ and is usually represented as $Cu(en)_2(OH)_2$.

Jolley,[76] in attempting to determine the structure of cuprammonium complexes, also worked with the analogous diamine compounds. The conditions employed were essentially the same as for cuprammonium in which the concentration of copper was too low to effect complete solution of the cellulose, so that the concentration of copper and diamine could be determined in both the solid and solution phases. Jolley confirmed the observation that the diamines are different from ammonia in that the addition of excess ammonia to cuprammonium solutions increases the solvent action of the solution, whereas the addition of excess diamine decreases the solvent action. In copper hydroxide-ethylenediamine solutions in which the concentration of diamine was varied from 6 to 210 g. per liter, the ratio of ethylenediamine to copper was not 2:1 but varied between 1.9 and 1.78:1. Jolley concluded, as had Hoffmann,[77] that both the monodiamine complex $[Cu(en)(OH)_2]$ and the di-diamine complex $[Cu(en)_2(OH)_2]$ were formed in the copper hydroxide-diamine system. Furthermore, it was shown that, in solutions of partially dissolved cotton, the ratio of copper

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[73] A. J. Stamm, *J. Am. Chem. Soc.*, **52**, 3047, 3062 (1930).

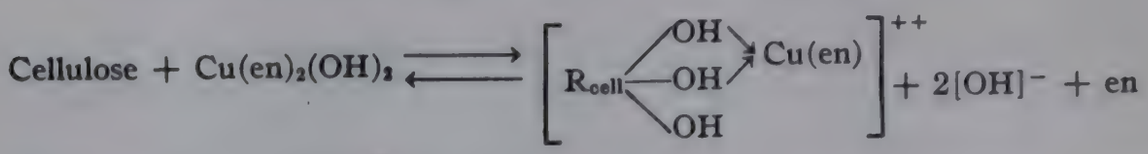
[74] E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 153 (1935); E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

[75] E. Berl and A. G. Innes, *Z. angew. Chem.*, **23**, 987 (1910).

[76] L. J. Jolley, *J. Textile Inst.*, **30**, T22 (1939).

[77] H. Hoffmann and N. Bruch, *Cellulosechem.*, **14**, 50 (1933).

to diamine in the undissolved fibers was unity. As a result of a careful study of this system, Jolley proposed the following mechanism for the solution of cellulose in copper hydroxide-diamine solutions:



In this formulation the ratio of copper to diamine in the cellulose complex is also unity. The primary importance of Jolley's work was to point out the differences between the diamine and ammonia systems and to emphasize the fact that conclusions reached from a study of the cellulose-copper hydroxide-diamine system could not necessarily be applied to the similar cuprammonium system.

The cuprammonium-cellulose system is complicated still further from the viewpoint of establishing a reaction mechanism by the addition of inorganic bases such as sodium, potassium, or lithium hydroxides to the solution. It was shown by the work of Traube, Hess, and Trogus and Sakurada[78] that the addition of small amounts (1 to 3%) of alkali hydroxides to cellulose increases its solubility in cuprammonium solutions. It is not known exactly how the sodium ions enter the cuprammonium-cellulose complex, but the most plausible mechanism is that they replace a portion of the $[Cu(NH_3)_4]^{++}$ ions in the cation part of the molecule. Additional evidence for this view was obtained by Jolley,[76] who showed that cellulose reacts with copper hydroxide in the presence of sodium, lithium, and potassium hydroxides to form a cellulose-copper complex but that the complex is not soluble in aqueous solutions of these bases.

In spite of all the investigations that have been carried out in this field, the exact mechanism by which cuprammonium solution dissolves cellulose is not known. The evidence indicates that the positive $[Cu(NH_3)_4]^{++}$ ion combines with the hydroxyl groups in cellulose in the ratio of approximately one mole of copper per each mole of cellulose in standard cuprammonium solutions. The reaction of cuprammonium solution with cellulose fibers is certainly heterogeneous in that the surface molecules of the structure are first attacked. The solution of the surface molecules then exposes new surfaces for further reaction. Although cuprammonium solution is unstable and is relatively difficult to prepare, it is still one of the most useful tools for characterizing cellulose.

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[78] C. Trogus and I. Sakurada, *Ber.*, **63B**, 2174 (1930)

4. Cellulose-Organic Base Complexes

The reaction of cellulose with organic bases has been primarily of academic interest. However, some of the tetraalkylammonium bases recently have become commercially available. Dehnert and König[79] showed that certain organic bases such as tetraalkylammonium bases,

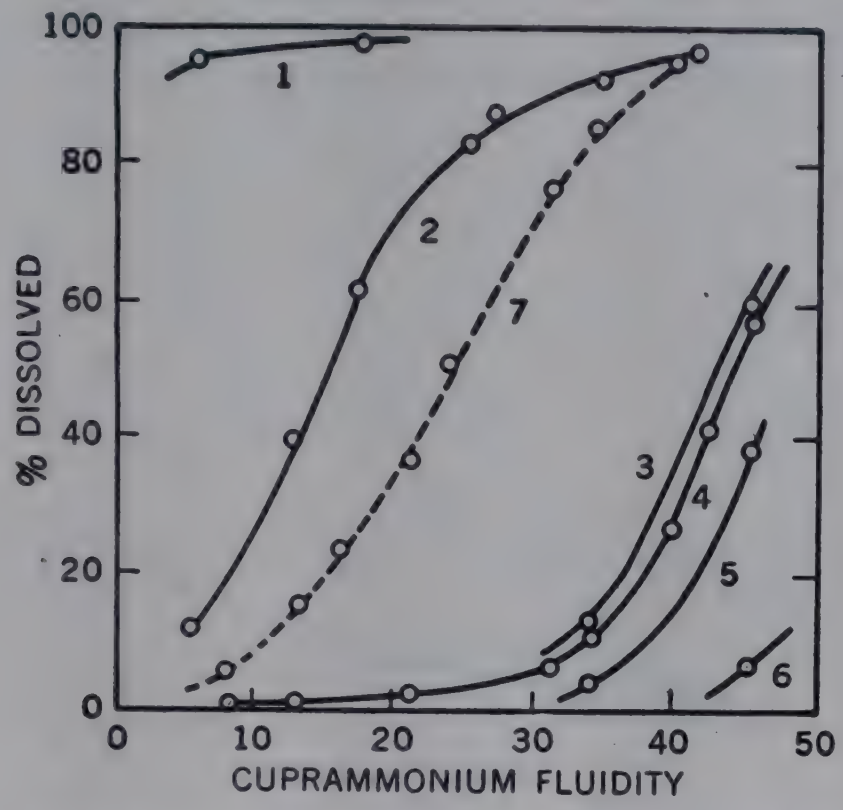

FIG. 31.—RELATION BETWEEN FLUIDITY OF MODIFIED COTTONS AND THEIR FRACTIONAL SOLUBILITY IN DIFFERENT BASES AT THEIR OPTIMUM CONCENTRATIONS (BROWNSETT AND CLIBBENS[80]).

Curves: 1, dibenzyldimethylammonium hydroxide at 20°C.; 2, benzyltrimethylammonium hydroxide at 20°C.; 3, tetramethylammonium hydroxide at 15°C.; 4, NaOH at 15°C.; 5, LiOH at 15°C.; 6, KOH at 15°C.; 7, NaOH at −5°C.

R_4NOH, and guanidinium hydroxide, $[(NH_2)_3C]OH$, are strong swelling agents for cellulose. Hess and Trogus[81] investigated the action of a number of other organic bases, such as hydrazine, ethylenediamine, and tetraethylenediamine, on cellulose and concluded from x-ray studies that these bases form definite compounds with cellulose.

Lieser and Leckzyck[82] concluded from a study of the action of tetraalkylammonium bases on celluloses that the tetraalkyl bases having a

[79] F. Dehnert and W. König, *Cellulosechem.*, **5**, 107 (1924); **6**, 1 (1925).
[80] T. Brownsett and D. A. Clibbens, *J. Textile Inst.*, **32**, T32, T57 (1941).
[81] K. Hess and C. Trogus, *Z. physik. Chem.*, **B14**, 387 (1931).
[82] T. Lieser and E. Leckzyck, *Ann.*, **522**, 56 (1936).

molecular weight of approximately 150 or greater are solvents for cellulose, whereas the lower-molecular-weight bases are only swelling agents. They showed also that each base has a specific concentration at which it is most effective as a solvent for cellulose, and that this concentration decreases as the molecular weight of the base increases. Brownsett and Clibbens[80] confirmed the work of Lieser and Leckzyck and showed that the maximum solubility of cellulose in aqueous solutions of tetramethyl-, benzyltrimethyl-, and dibenzyldimethyl-ammonium hydroxides occurs at 2.5 *N*, 2.15 *N*, and

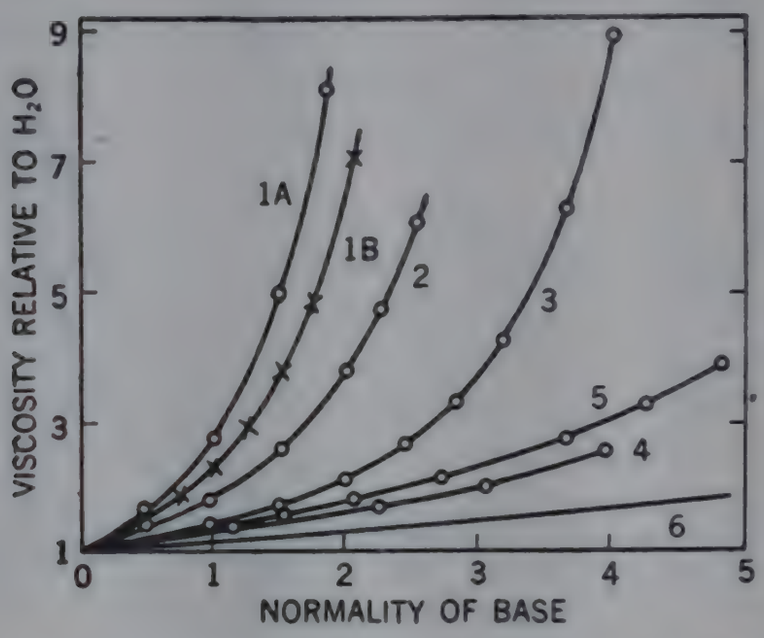

FIG. 32.—RELATIVE VISCOSITIES OF AQUEOUS SOLUTIONS OF DIFFERENT BASES AT 20 °C. (BROWNSETT AND CLIBBENS[80]).

Curves: 1, dibenzyldimethylammonium hydroxide (samples A and B); 2, benzyltrimethylammonium hydroxide; 3, tetramethylammonium hydroxide; 4, NaOH; 5, LiOH; 6, KOH.

1.9 *N*, respectively. These workers also pointed out that there is a relationship between solvent activity and the relative viscosity of the organic bases. Thus, dibenzyldimethylammonium hydroxide, which has the greatest solvent action on cellulose, also possesses the highest relative viscosity (Figs. 31 and 32). The high-molecular-weight tetraalkyl bases, such as dibenzyldimethylammonium hydroxide, approach cuprammonium hydroxide in solvent action, since they are capable of dissolving relatively undegraded cotton linters and wood pulp fibers. The wide utilization of these bases in cellulose reactions has been limited primarily by their high cost in comparison with the inorganic bases such as sodium hydroxide.

The reactions of cellulose in aqueous solutions of the organic bases are,

In general, similar to reactions in solutions of inorganic bases with the exception that in the organic bases the reactions can be carried out in homogeneous media. Lieser and Leckzyck[82] were able to prepare the trixanthate of cellulose by treating cellulose with carbon disulfide in a 3.7 *M* solution of tetraethylammonium hydroxide. Likewise, Powers and Bock[83] were able to prepare the substituted acetals and ethers of cellulose by treating cellulose dissolved in tetraalkylammonium bases with α-chloro ethers and alkyl chlorides, respectively. One possible advantage of the organic over the inorganic bases as reaction media for cellulose reactions is that more uniform partially-substituted derivatives may be obtained, since the reactions in organic bases can be carried out in a homogeneous system. Mahoney and Purves[84] have confirmed this possibility by showing that a partially ethylated cellulose prepared by a homogeneous reaction in an organic base is ethylated more uniformly than are similarly etherified celluloses prepared in the regular heterogeneous reaction from alkali cellulose.

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[83] L. H. Bock and A. L. Houk (to Röhm and Haas), U. S. Patent 2,083,554 (June 15, 1937); D. H. Powers, L. H. Bock, and A. L. Houk (to Röhm and Haas), U. S. Patent 2,087,549 (July 20, 1937).

[84] J. F. Mahoney and C. B. Purves, *J. Am. Chem. Soc.*, **64**, 9 (1942).

E. CELLULOSE ETHERS

SHAILER L. BASS, A. J. BARRY, AND A. E. YOUNG

The ethers of cellulose are the most recent arrivals in the family of cellulose derivatives and constitute one of the most interesting developments of cellulose chemistry in the present century.[1] Their preparation and applications have been accorded a lively industrial interest as evidenced by the voluminous patent literature.[2] Academic interest in cellulose ethers, especially in the methyl, ethyl, and benzyl ethers, has been centered in their use as a tool to advance the knowledge of the chemistry, structure, and reactions of cellulose (see Chapter II).

These two fields of cellulose ether endeavor, industrial production and fundamental research, have merged in recent years, as evidenced by published accounts of careful experimental work on which issued patent applications have been based. This is especially the case in the United States, where certain ethers of cellulose have begun to reach industrial maturity.

The growth and industrial development of cellulose ethers in this country, particularly the ethyl, methyl, hydroxyethyl, and carboxymethyl ethers, has been founded upon the economic availability of the required etherifying agents, the greatly improved knowledge of the chemistry of cellulose, and the widely diversified applications to which the properties of these ethers have led.

1. History

Cellulose ethers were conceived in 1905 by Suida,[3] who was first to describe the theoretical basis of etherification. Suida assumed that cellulose had the nature of an anhydride alcohol whose active groups were alcoholic hydroxyls. He thought that at least some were endowed with acidic properties in view of the known existence of alkali cellulose. He considered that these active hydroxyls were responsible for the absorption of dyestuffs

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[1] D. Traill, *J. Soc. Chem. Ind.*, **53**, 337T (1934).

[2] E. C. Worden, *Technology of Cellulose Ethers*. Vols. I and III, Worden Laboratory and Library, Millburn, N. J., 1933.

[3] W. Suida, *Monatsh.*, **26**, 413 (1905).

by cellulose and attempted to prove it by inactivating them in the form of ethers or esters. For his purpose, however, the etherification was limited to a surface reaction of dimethyl sulfate upon an alkali swollen cellulose and did not yield a cellulose ether in the sense of a separate chemical entity. This early attempt to modify cellulose fibers has since given rise to a variety of surface etherifications of cotton fibers and textiles to produce special effects.[4]

The technical development of cellulose ethers dates from 1912 with the contemporaneous filing of patents by Leuchs,[5] Dreyfus,[6] and Lilienfeld.[7] All three inventors directed their attention primarily to the preparation of alkyl ethers highly enough substituted to be soluble in organic solvents, except Lilienfeld, who also claimed and later described[8] ethers soluble in cold water but insoluble in or only swelled by hot water.

Essentially, cellulose or regenerated cellulose was swollen in aqueous alkalies and caused to react with an alkyl chloride or sulfate to form ethers of varying degrees of substitution and solubility. Both Leuchs and Dreyfus realized the importance of reducing the water content of the alkali cellulose, and all three mentioned the use of water-immiscible organic diluents for the etherifying agent. Dreyfus pointed out that the diluent could help direct the course of the reaction and could dissolve the reaction product. Leuchs and Lilienfeld called attention to the possibility of forming mixed ethers and etherified celluloses of different degrees of substitution. These three patents signaled the start of a race for technological development in the alkyl ethers of cellulose which has been recorded in chronological detail by Worden.[2]

While these patents were pending, Denham and Woodhouse[9] described the methylation of cellulose in considerable detail. Their work was directed toward preparing trimethylcellulose for use in establishing the structure of cellulose, and the preparation of ethers of lower substitution[9, 10]

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[4] See, for example, L. Lilienfeld, U. S. Patents 1,736,714 (Nov. 19, 1929); 1,800,944 (Apr. 14, 1931); R. Haller and A. Heckendorn (to Soc. Chem. Ind., Basle), U. S. Patent 1,879,742 (Sept. 27, 1932); L. G. Lawrie, R. J. W. Reynolds, and D. Ward, *J. Soc. Dyers Colourists*, **56**, 6 (1940).

[5] O. Leuchs (to Bayer and Co.), German Patent 322,586 (filed Jan. 26, 1912, issued July 1, 1920).

[6] H. Dreyfus, French Patent 462,274 (filed Nov. 18, 1912; issued Jan. 23, 1914).

[7] L. Lilienfeld, Brit. Patent 12,854 (filed May 31, 1912; issued Sept. 1, 1913); U. S. Patent 1,188,376 (filed June 26, 1912; issued June 20, 1916).

[8] L. Lilienfeld, U. S. Patent 1,683,831 (Sept. 11, 1928).

[9] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **103**, 1735 (1913).

[10] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **105**, 2357 (1914).

was incidental. There followed the quantitative hydrolysis of trimethyl cellulose to 2,3,6-trimethylglucose[11, 12] which is now accepted as classical proof that all the glucose units in alpha-cellulose are identical and that substitution on cellulose occurs only on the 2-, 3-, and 6- positions. Haworth's chemical proof[13, 14] of the structure of the glucose residue and its method of linking in cellulose, together with x-ray evidence, led shortly afterward to the establishment of the fact that anhydro-β-glucose is the repeating unit in the cellulose chain molecule.[15] (See also Chapter II, B.)

In their research on the constitution of cellulose, Haworth and coworkers used a novel method of preparing highly methylated cellulose. It consisted in subjecting cellulose acetate to simultaneous saponification and methylation by treating it in acetone solution with aqueous caustic and dimethyl sulfate.[16]

The classical reaction of diazomethane with hydroxyl groups was applied to cellulose in 1914 by Nierenstein[17] and has recently been studied more extensively by Reeves and Thompson.[18]

More recently, the classical reaction of sodium with alcoholic hydroxyls has been applied successfully to the preparation of cellulose ethers by Peterson and Barry.[19, 20] Cellulose is swollen in liquid ammonia and reacted with sodium or sodamide to form sodium cellulosate. The lower alkyl chlorides and bromides are sufficiently soluble in liquid ammonia and react slowly enough with it at low temperatures to permit highly efficient alkylation of cellulose.

2. Chemistry of the Etherification Reaction

Except for ethylene oxide and its homologs (see p. 762) which enter into direct addition with cellulosic hydroxyls, and for the special cases of methylation with diazomethane (see p. 764) and alkylations in liquid ammonia, the etherification of cellulose takes place by interaction of an organic ester with a swelling compound of cellulose and an aqueous base. The base

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[11] W. S. Denham, *J. Chem. Soc.*, **119,** 77 (1921).
[12] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **123,** 519 (1923).
[13] W. N. Haworth, *Nature*, **116,** 430 (1925); *J. Chem. Soc.*, **1926,** 89.
[14] W. N. Haworth and H. Machemer, *Ber.*, **65B,** 60 (1932).
[15] H. Mark, *Chem. Revs.*, **26,** 178 (1940).
[16] W. N. Haworth, E. L. Hirst, and H. A. Thomas, *J. Chem. Soc.*, **1931,** 821.
[17] M. Nierenstein, *Ber.*, **58B,** 2615 (1925); *Helv. Chim. Acta*, **92,** 150 (1914).
[18] R. E. Reeves and H. J. Thompson, *Contrib. Boyce Thompson Inst.*, **11,** 55 (1939).
[19] A. J. Barry, F. C. Peterson, and A. J. King, *J. Am. Chem. Soc.*, **58,** 333 (1936).
[20] F. C. Peterson and A. J. Barry (to Dow Chemical Co.), U. S. Patents 2,145,273 (Jan. 31, 1939); 2,157,083 (May 2, 1939); 2,232,926-7 (Feb. 25, 1941).

may be organic, as in alkylations of cellulose in quaternary bases, but is usually inorganic. The use of inorganic bases other than sodium hydroxide has been described,[21] but this still remains the alkali used in commercial practice.

(*a*) *Etherifying Agents*

In the preparation of a given cellulose ether, the efficiency of the reaction is considerably dependent upon what ester is used as the alkylating agent. Among the alkyl halides, the classical order of reactivity is that of decreasing degree from iodide to bromide to chloride. On account of the heterogeneous nature of the reaction with cellulose, this order is altered. Since the cellulosic hydroxyls are generally in a solid phase and are surrounded by a solvating medium which, in most cases, is an aqueous solution of sodium hydroxide, the etherifying agent must dissolve in the caustic and diffuse to the reaction centers.[22] The slow diffusion rate of methyl iodide and its high reactivity make it less efficient as a methylating agent than either methyl bromide or methyl chloride because it is largely converted to by-products. However, alkyl chlorides are preferred to bromides in commercial practice because the small advantage in reactivity of the bromides is more than offset by their greater cost.

Alkyl sulfates and phosphates have found little commercial utility because of their cost and high rate of saponification, although sodium methyl or ethyl sulfate have some interest in the preparation of ethers of low substitution because of their solubility in water and aqueous alkalies.[23]

The ease of etherification is a direct function of the rate of diffusion of the etherifying agent into the swollen alkali cellulose.[24, 25] Diffusion and solubility depend upon molecular size, as shown by the fact that methyl and ethyl chloride diffuse readily into the swollen fiber and that alkylation becomes progressively more difficult with the higher alkyl chlorides. In the series of alkyl chlorides, the solubility in aqueous sodium hydroxide decreases with increasing molecular size and with increasing caustic concentration.

The primary alkyl chlorides containing three or more carbon atoms have not yielded useful water-soluble or alkali-soluble ethers, probably because of

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[21] H. Dreyfus, U. S. Patents 2,098,335 (Nov. 9, 1937); 2,181,264 (Nov. 28, 1939).

[22] E. J. Lorand and E. A. Georgi, *J. Am. Chem. Soc.*, **59**, 1166 (1937).

[23] R. W. Maxwell (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,101,263 (Dec. 7, 1937).

[24] E. J. Lorand, *Ind. Eng. Chem.*, **31**, 891 (1939).

[25] K. Hess, C. Trogus, W. Eveking, and E. Garthe, *Ann.*, **506**, 260 (1933).

their more hydrophobic character together with the difficulty of introducing them uniformly enough throughout the fiber. When used to prepare organo-soluble ethers from alkali cellulose, these reagents are sensitive to the strong alkali and to the higher etherification temperature which are necessary. Besides causing greater saponification of alkylating agent, the higher temperature increases degradation of the cellulose so that the resultant ethers are usually very low in viscosity. The principal interest in the higher alkyl halides, therefore, resides in their use to prepare mixed ethers with methylcellulose or ethylcellulose.[26, 27]

Steric hindrance also affects the choice of an alkylating agent. For example, in the reaction of isopropyl chloride with alkali cellulose, the amount of etherification is slight compared to the formation of by-products; and triply branched bulky molecules, like *tert*-butyl chloride, are entirely converted to by-products.

Chlorides also are generally used to introduce other etherifying radicals such as benzyl, carboxymethyl, and hydroxyethyl. In the last case, however, direct addition of ethylene oxide can be used, a reaction which is analogous to the formation of cellulose acetate by the addition of ketene to cellulosic hydroxyls. Diazomethane is principally interesting as a methylating agent for the information it gives about the availability for etherification of hydroxyl groups in the amorphous regions of cellulose (see p. 765).

(*b*) *Alkali Cellulose Composition*

For a single cellulosic hydroxyl, the reaction may be pictured by equation (1).

$$[R_{cell}\text{—}OH \cdot NaOH \rightleftharpoons R_{cell}\text{—}ONa \cdot H_2O] + RX \rightarrow R_{cell}\text{—}OR + NaX + H_2O \qquad (1)$$

Whether the NaOH is considered to be associated with the cellulosic hydroxyl or reacts with it to form an alkali cellulosate, in the cellulose swelling compound present in alkali cellulose an excess of water over that postulated in equation (1) is required in actual practice. The presence of water serves two necessary functions: (1) it acts as a solvent and carrier for caustic, distributing it around the hydroxyl reaction centers, and (2) it acts as a solvating or swelling agent for the alkali cellulose, loosening up the structure so that the etherifying agent can penetrate the fiber.[24]

The optimum ratios of caustic to cellulose and of water to cellulose must be determined to obtain the degree of substitution desired with each

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[26] M. Hagedorn and P. Möller, *Cellulosechem.*, **12**, 29 (1931).

[27] J. F. Haskins and D. C. Ellsworth (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,102,205 (Dec. 14, 1937).

etherifying agent. They are also influenced to some extent by other factors such as the presence of diluents, the kind and amount of agitation, and the temperature schedule. In spite of advances in the fundamental knowledge of cellulose and its derivatives, the etherification of cellulose still remains an art that is learned by experience, and its products are duplicated only from a detailed familiarity with the effects of all reaction variables involved.

In the commercial production of cellulose ethers, the composition of alkali cellulose and its uniformity are very closely controlled. Increasing the NaOH : H_2O ratio increases the speed of the reaction and the degree of substitution, which also depends upon a low H_2O: cellulose ratio. The proportion of etherifying agent going to side reactions is increased as the H_2O:cellulose ratio increases, but the by-products obtained are influenced by the NaOH:H_2O ratio; ether predominates when this ratio is high and alcohol when it is low.[24]

(c) The Etherification Reaction as Conditioned by the Structure of Cellulose

The hydroxyl groups in the anhydroglucose units of cellulose have been etherified by all of the reactions classically employed for etherifying the monomeric polyhydric alcohols. In the etherification of cellulose, however, the reaction is always a heterogeneous one and is conditioned by any or all of the structural units existing in the cellulose fiber.

Effect of Crystalline Structure. Fibrous cellulose is now generally considered to contain elongated crystallites in which the individual long-chain macromolecules of anhydroglucose units exist in a highly ordered arrangement.[15, 28, 29] The strongest forces holding the cellulose molecules together act along the fiber axis where primary valence forces tend to keep the glucose units linked into long molecules throughout the etherification reaction.

These long-chain molecules exist in space in a closely packed structure. The attractive forces holding the chains laterally oriented in this arrangement are considered to exist between oxygen atoms of neighboring chains. Since certain oxygen atoms can approach each other more closely than would be expected if only the normally attractive, or van der Waals', forces were acting, a stronger bonding force must exist between them.[15] This has been assumed to be a hydrogen bond or bridge.[30, 31] This subject is discussed fully in Chapter III, A.

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[28] W. A. Sisson, *Ind. Eng. Chem.*, **30,** 530 (1938).
[29] E. Sauter, *Z. physik. Chem.*, **B35,** 117 (1937).
[30] M. L. Huggins, *J. Org. Chem.*, **1,** 407 (1936).
[31] J. W. Ellis and J. Bath, *J. Am. Chem. Soc.*, **62,** 2859 (1940).

Effect of Submicrostructure. The crystallites of rigid closely packed cellulose chain molecules do not make up the total structure of the fiber. They are no longer thought to exist as separate and distinct units but are believed to grade continuously into amorphous regions through which the chains extend in less orderly arrangement.[28, 29]

This intercrystalline material makes up a considerable portion of the fiber and is thought to permeate the submicrostructure of the fiber[29, 32] (see Chapter III, A, C, and E). Through it runs a meshwork of fine capillaries or voids ranging in cross section down to molecular size.[33] They are thought to occupy only a small proportion of the volume of the total fiber and to be open to most liquids. Passageways are thus provided throughout the fine structure of the fiber to allow cellulose swelling agents to penetrate the amorphous regions and, eventually, the crystallites.[34]

Surface Etherification. It has been proposed to determine the cellulosic hydroxyls available on these internal surfaces by methylation. Harris and Purves[33] reacted bone-dry ramie fibers with an ethereal solution of thallium ethylate followed by methyl iodide as shown in equations (2) and (3).

$$R_{cell}—OH + TlOC_2H_5 \rightarrow R_{cell}—OTl + C_2H_5OH \qquad (2)$$

$$R_{cell}—OTl + CH_3I \rightarrow R_{cell}—OCH_3 + TlI \qquad (3)$$

Purified ramie gave 0.14% methoxyl and a mercerized ramie 10.3% methoxyl.

Reeves and Thompson[18] treated raw native cotton and mercerized cotton with diazomethane dissolved in ether (equation (4)).

$$R_{cell}—OH + CH_2N_2 \rightarrow R_{cell}—OCH_3 + N_2 \qquad (4)$$

Their results, given in Table 1, show very low degrees of methylation for the vacuum-dried fibers and a marked increase in the degrees of methylation with small changes in the moisture content of the fiber.

The data of Table 1, together with x-ray examination of the products,[18] indicate that the presence of moisture increased the availability of hydroxyl groups in the intercrystalline material and that, for a given moisture content, there was a limit to the number of hydroxyls so made available for reaction. This greater ease of accessibility of cellulose in the amorphous

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[32] A. Frey-Wyssling, *Protoplasma*, **25**, 261 (1936).

[33] C. A. Harris and C. B. Purves, *Paper Trade J.*, **110**, 29 (Feb. 8, 1940).

[34] H. M. Spurlin, *Trans. Electrochem. Soc.*, **73**, 95 (1938).

regions undoubtedly plays a considerable part in etherifications in the presence of aqueous bases which can also swell the crystalline regions.

The methylated products of Reeves and Thompson[18] represent what is probably one extreme in heterogeneity of etherification. The fact that

TABLE 1

INFLUENCE OF FIBER MOISTURE CONTENT ON THE METHYLATION OF CELLULOSE WITH DIAZOMETHANE (REEVES AND THOMPSON[18])

(0.2 g. fiber in 20 cc. of 0.5 *M* ethereal CH_2N_2)

Pretreatment of fiber	Raw native fiber		Mercerized fiber	
	% moisture before methylation	% methoxyl after one treatment[a]	% moisture before methylation	% methoxyl after one treatment[a]
Dried *in vacuo* at 100°C. over P_2O_5	0.00	0.25	0.00	0.48
Dried at room temp. over $CaCl_2$	2.0	4.0	4.7	9.0
Air-dried[b]	4.18	4.4	7.0	11.5
Five days in moist chamber	6.1	5.3	9.1	12.6

[a] One week standing at 0°C.

[b] Seven repeated treatments reached constant methoxyl content at 9.8% (D.S. = 0.5) for raw cotton and 17.8% (D.S. = 1.0) for mercerized cotton. (The x-ray pattern of the latter shows crystallinity in contrast with the completely amorphous pattern of methylcellulose of 18.2% methoxyl prepared in dibenzyldimethylammonium hydroxide.) These partially methylated fibers were all soluble in cuprammonium solution but not dispersed by alkalies.

they still retained the solubility properties of cellulose indicates that cellulose ethers exhibiting smooth solubility behavior in dilute alkalies, water, or organic solvents will not be obtained until the cellulose chains in the crystallites have themselves been etherified to the desired degree of substitution.

Swelling Agents. In order to provide space for introducing etherifying radicals into the closely packed structure of the crystallites, they must also be distended by cellulose swelling agents. These act to distend the lattice by aiding the process of solvation around the cellulosic hydroxyls as centers. The forces between the hydroxyls of neighboring chains are broken, and the hydroxyls become available for reaction. Another function of the swelling agent is to expand the fiber, thereby aiding the diffusion of the etherifying agent to all parts of it.

The swelling agents most important to the discussion of cellulose ethers are aqueous caustic soda (see Section D of this chapter), aqueous NaOH in conjunction with $Cu(OH)_2$,[35–41] solutions of quaternary bases,[41, 42, 43] and sodium or sodamide in liquid ammonia.[19, 20] All these act to distend the unit cell to varying degrees, depending upon their respective molecular volumes[19, 37, 41] (see also Section D of this chapter) and upon the amount of swelling.[43]

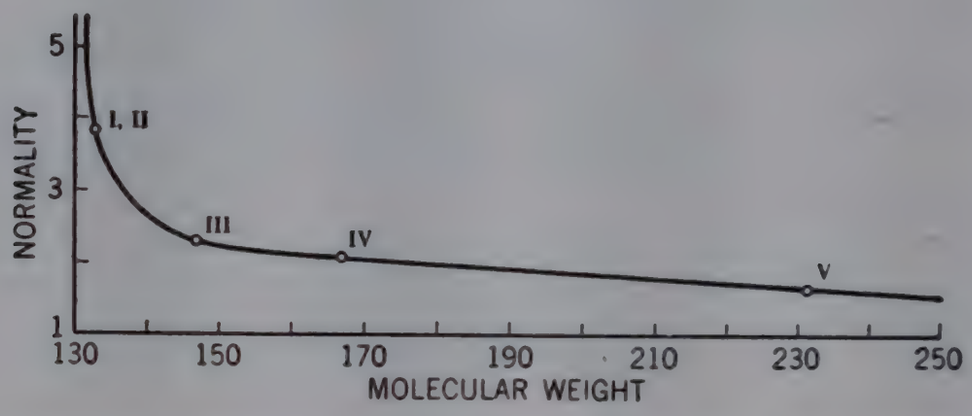

FIG. 33.—MINIMUM NORMALITY OF QUATERNARY AMMONIUM HYDROXIDE SOLUTIONS REQUIRED TO DISPERSE CELLULOSE (LIESER[37]).

	Quaternary Base	Molecular Weight
I.	$(CH_3)_3C_4H_9NOH$	133
II.	$(C_2H_5)_3CH_3NOH$	133
III.	$(C_2H_5)_4NOH$	147
IV.	$(CH_3)_3C_6H_5CH_2NOH$	167
V.	$(C_4H_9)_3C_2H_5NOH$	231

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[35] W. Traube and A. Funk, *Ber.*, **69B**, 1476 (1936).

[36] W. Traube, R. Piwonka, and A. Funk, *Ber.*, **69B**, 1483 (1936).

[37] T. Lieser, *Ann.*, **528**, 276 (1937).

[38] W. Traube (to "Achetem"), U. S. Patent 2,140,568 (Dec. 20, 1938).

[39] R. Piwonka, *Ber.*, **69B**, 1965 (1936).

[40] H. Schenck, Dissertation, Berlin, 1936, p. 25 *et seq.*

[41] W. A. Sisson and W. R. Saner, *J. Phys. Chem.*, **43**, 687 (1939).

[42] L. H. Bock, *Ind. Eng. Chem.*, **29**, 985 (1937).

[43] T. Brownsett and D. A. Clibbens, *J. Textile Inst.*, **32**, T32 (1941).

When the swelling agent is an aqueous base, the etherification is usually carried out in the presence of a considerable excess of the base. When the swelling agent is liquid ammonia, three equivalents of metallic sodium are usually introduced in the cellulose before subjecting it to the action of etherifying agents.[20]

Certain quaternary bases of high molecular weight cause a large and limited distention of the cellulose crystallites but produce an unlimited swelling of the amorphous material.[41] When present in excess, they eventually cause the dispersion of the entire fiber. The amount of distention of the crystallite lattice and the normality of base required for complete dispersion are associated with the molecular volume of the solvated base[37, 41] as shown by the curve of Figure 33.

In any strong base, however, the swelling of cellulose results in at least partial solution of the lower-chain-length molecules. The dissolved fraction consists of all the chain lengths below a limiting length which is determined by the degree of swelling. The greater the swelling, the higher is the upper limit to the length of the chains which can be dispersed.[43]

This partial solubility of cellulose in the base used and the consequent greater availability of the hydroxyls of the shorter chains for etherification probably accounts for the fact that, in the fractionation of cellulose ethers, the lowest viscosity fractions show the highest degrees of substitution. This is the case not only for organo-soluble ethylcellulose[44] but also for water-soluble methylcellulose.[45]

Alkali Cellulose. The reaction of the hydroxyl groups of individual glucose units with an etherifying agent is generally considered to occur through an intermediate solvated alkali cellulose in which the acidic hydrogens of the glucose hydroxyls are in equilibrium with sodium or other basic radicals. The degree to which the cellulosic hydroxyls approach complete etherification must be a function of the proportion of cellulosic hydroxyls in such equilibrium in any given molecular layer in the intermediate swelling compound. In aqueous bases, this depends upon the mass action effect of the molar concentration of the base.

Thus, the over-all driving power for the etherification of cellulose in aqueous base systems is the concentration of the base used as a swelling agent and maintained throughout the reaction. This is indicated by the

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[44] Dow Chemical Co., unpublished data.

[45] R. Signer and J. Liechti, *Helv. Chim. Acta*, **21**, 530 (1938).

observation that the rate of etherification is some high power of the concentration of alkali,[46] and by the fact that the ethoxyl content of a series of ethylcellulose preparations increased with the concentration of base at the end of the reaction.[24] It is also shown by the difficulty of early investigators of obtaining very high degrees of methylation using 15% to 18% NaOH (see p. 788). Actually, the preparation of highly methylated or ethylated cellulose is not difficult if the caustic concentration is kept high.[24, 46, 47]

Necessity of Solvating Agent. The fact that etherification does not occur in the absence of a solvating agent is shown by the following experiment. Solvate-free sodium cellulosate was prepared by treating cellulose in liquid ammonia with three equivalents of sodium and allowing the ammonia to boil off under anhydrous conditions. When this product was heated in excess ethyl chloride, little or no etherification occurred, but the addition of about six moles of water to the system allowed conversion to ethylcellulose.[44] The solvating agent can be liquid ammonia instead of water as shown by the fact that when the trisodium cellulosate was allowed to remain in liquid ammonia, it could be methylated to a high degree of substitution[48] (D.S. 2.85) by a stoichiometrical amount of methyl bromide.[20, 44] There is also at least one case in which the solvating agent is indicated to be methanol[47] (see p. 776).

Randomness of Etherification. The etherification of cellulose must also be considered from the point of view that the cellulose chain molecule is a large structural unit along which the substituent groups will be distributed among the available positions according to the laws of chance. The statistical distribution of substituting groups was calculated by Spurlin[46] from the premise that the ratio of the reactivities of the 2-, 3-, and 6-hydroxyl groups, either of any particular glucose unit or of the chain as a unit, remains independent of the degree of substitution throughout the reaction, however much the reactivity of the whole may vary. The fraction of the total number of glucose units which will contain 0, 1, 2, or 3 substituents is given by the curves of Figure 34 for several arbitrarily chosen ratios of equilibrium or rate constants.[46]

The curves of Figure 34 express the maximum randomness of distribution

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[46] H. M. Spurlin, *J. Am. Chem. Soc.*, **61**, 2222 (1939).

[47] K. Hess and C. Trogus, *Z. physik. Chem.*, **B15**, 157 (1932).

[48] D.S. is used throughout this section as an abbreviation for degree of substitution.

which can be expected if all the chains in any given cross section of cellulose fiber are exposed equally to etherifying conditions of the same driving power. The curves therefore indicate the ultimate that may be expected in uniformity of substitution throughout the gross structure of the fiber as etherification conditions approach those of a homogeneous reaction.

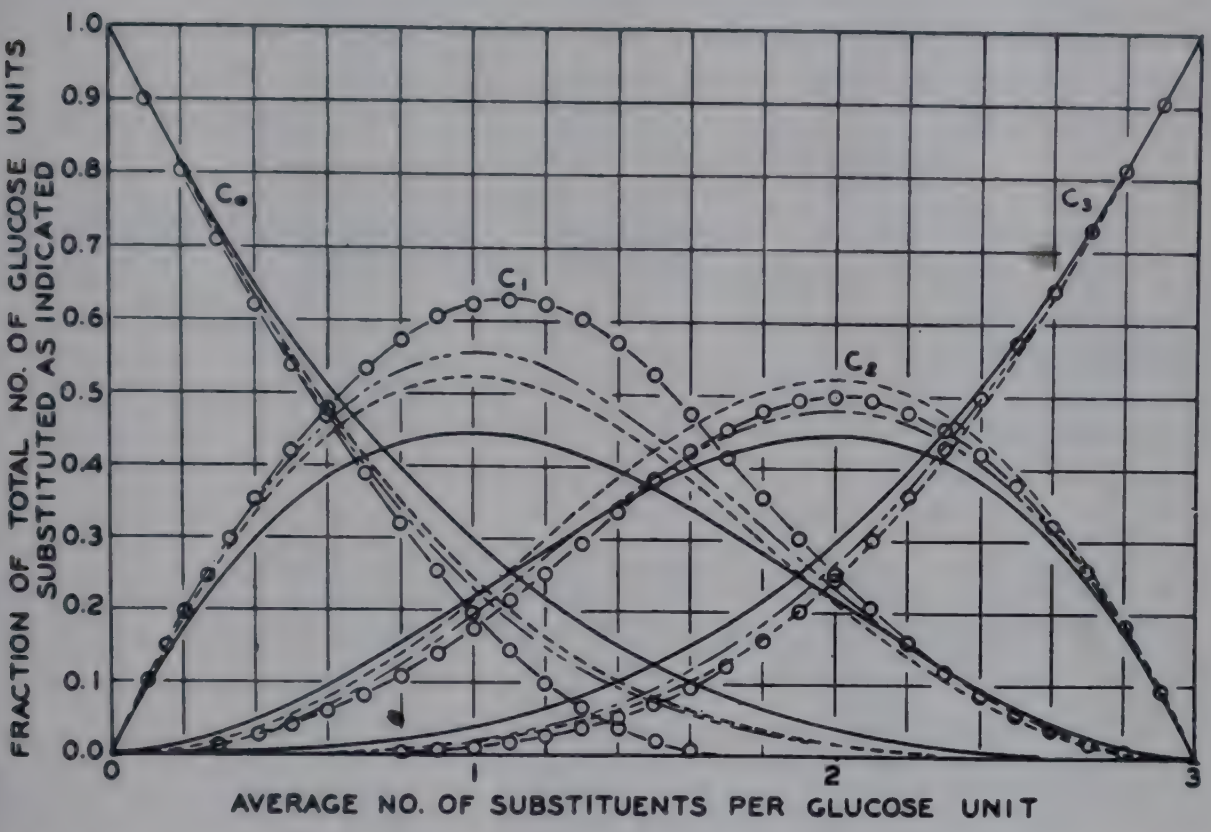

FIG. 34.—THEORETICAL OVER-ALL DISTRIBUTION OF SUBSTITUENT GROUPS ON CELLULOSE (SPURLIN[46]).

C_0—Unsubstituted.
C_1—Monosubstituted.
C_2—Disubstituted.
C_3—Trisubstituted.

Ratio of Equilibrium Constants
——— 1:1:1
– – – – 1:4:16
— – – 1:1:10

Ratio of Rate Constants
——— 1:1:1
–o— 1:1:10

Quasi-Homogeneous Etherification. One approach to this condition of equal availability of all the cellulosic hydroxyls to etherification is probably exhibited by the dispersions of cellulose in quaternary bases of high molecular volume.[41, 42] These bases react to form a "swelling compound" or complex with the cellulose crystallites and, when present in sufficient excess, continue the swelling to eventual complete dispersion of the

fibers.[49, 50, 51] Sisson and Saner found that the x-ray pattern of the swelling compound formed with insufficient base to cause dispersion indicated an apparently equal modification of all the crystalline material,[41] a condition which is characteristic of quasi-homogeneous or permutoid reactions.[22]

Each base has a minimum concentration below which the x-ray diagram of native cellulose is not affected[41] and an optimum concentration at which its fiber dispersing power reaches a maximum.[37, 41, 43] These are listed in Table 2.

TABLE 2

MINIMUM NORMALITY OF QUATERNARY BASE

Base	To distend cellulose lattice[41]	To dissolve cellulose completely[37, 51]	To dissolve max. % of cellulose[43]
$(CH_3)_4NOH$	2.0	...	...
$(CH_3)_3C_2H_5NOH$	1.9	3.8	...
$(C_2H_5)_4NOH$	...	2.3	...
$(CH_3)_3C_6H_5CH_2NOH$	1.6	2.1	2.15
$(CH_3)_2(C_6H_5CH_2)_2NOH$	1.15	...	1.9

The fact that a large normality of quaternary base is required for complete fiber dispersal indicates a mass action effect. Sisson and Saner[41] estimated that the increase in volume of the unit cell of cellulose is approximately that required for one molecule of quaternary base to be accommodated per glucose unit, but found that from 1.5 to 2.5 molecules of quaternary base per glucose unit must be present to effect a complete change in the x-ray diagram.

The larger the molecular volume of the quaternary base, the lower is the normality of its solution required to affect the cellulose x-ray diagram[41] or to produce complete dispersion of the fibers.[51] Bases having a molecular weight below about 130 produce only swelling without bringing the cellulose into solution. Bases of molecular weight above about 150 show a linear decrease in concentration minimum with increasing molecular weight (Fig. 33).

Methylation of the dispersion of cellulose in benzyltrimethylammonium hydroxide by dimethyl sulfate, which is soluble in the reaction mixture,

[49] D. H. Powers and L. H. Bock (to Röhm and Haas Co.), U. S. Patent 2,009,015 (July 23, 1935); L. H. Bock and A. L. Houk (to Röhm and Haas Co.), U. S. Patent 2,083,554 (June 15, 1937); D. H. Powers, L. H. Bock, and A. L. Houk (to Röhm and Haas Co.), U. S. Patent 2,087,549 (July 20, 1937).

[50] L. Lilienfeld, U. S. Patent 1,771,462 (July 29, 1930).

[51] T. Lieser and E. Leckzyck, *Ann.*, **522**, 56 (1936).

gave a methylcellulose of D.S. 0.7 which was apparently very uniformly methylated as judged by its reported solubility in water.[42] However, examination of its hydrolytic products indicated a random distribution of methyl groups among the glucose units[46, 52] which would be expected from the laws of probability.[46] This reaction becomes heterogeneous above D.S. 2.0 due to the insolubility of methylcellulose in the quaternary base.[53]

Ethylation of alpha-cellulose dispersed in benzyltrimethylammonium hydroxide yielded ethylcelluloses which were soluble in cold water at D.S. 0.6–1.2.[42, 49] Examination of a D.S. 0.58 ethylcellulose[54] showed the product to be difficultly dispersible in water and to be gelled on heating a 2% solution to 70°C.[44]

Bock[42] suggested that water solubility of the methylcelluloses or ethylcelluloses was due to unetherified hydroxyl groups made available for hydration because of the spacing apart of the individual cellulose chains by the respective ether groups. Relatively few ether groups would be required to separate the close packing of the cellulose chains provided they were uniformly distributed.

This does not mean regularity of substitution in the sense that every glucose unit carried an ether group as Bock's model suggested, since Compton[52] showed that methylcelluloses of D.S. 0.7–0.9 produced by dimethyl sulfate on cellulose in dibenzyldimethylammonium hydroxide consist of glucose units with 0, 1, and 2, and, to a small extent, even 3 methyl groups. This indicates that the distribution of methyl groups on cellulose dissolved in quaternary bases proceeds according to the laws of probability[46] just as in the case of sodium cupricellulose (see pp. 778 and 798). This is confirmed by chemical methods of analysis[54] of the distribution of the unetherified hydroxyl groups.

The meaning of uniformity of substitution when applied to partial etherification of homogeneously dispersed cellulose, whether in quaternary base or in sodium-copper complex, is probably that all hydroxyls along the chains are equally available for etherification,[54] not only those on the micellar surfaces but also those within the micelles.[37] In a macroheterogeneous reaction, such as the methylation of alkali cellulose, this can never be the case, and the reaction must depend upon substitution of methyl groups for hydroxyls upon the micellar surfaces to open up the way for penetration of etherifying agent and perhaps also of alkali to the hydroxyls of the intermicellar surfaces. Thus, when water solubility is finally attained, the outer

[52] J. Compton, *J. Am. Chem. Soc.*, **60**, 2823 (1938).
[53] G. G. Johnston, *J. Am. Chem. Soc.*, **63**, 1043 (1941).
[54] J. F. Mahoney and C. B. Purves, *J. Am. Chem. Soc.*, **64**, 15 (1942).

hydroxyls of the micelles are more highly methylated than those of the interior.

Topochemical Macroheterogeneity. Superimposed upon the crystalline-amorphous heterogeneity, as disclosed by x-ray and fiber swelling evidence, is the microscopically observable lamination of cellulose due to growth layers. This has been demonstrated by Lorand and Georgi[22] in a study of the benzylation of cellulose. The immiscibility of the benzyl chloride with aqueous alkali further accentuates the heterogeneity of the system. Like most etherifications in aqueous alkali, it consists of three phases: cellulose, aqueous alkali, and etherifying agent.

The reaction in its early stages occurs at microscopically visible spots on the surface of the fiber, then spreads completely over the outside of the fiber, and proceeds inward progressively from one growth layer to the next. This is shown by photographs (Fig. 35) obtained by Lorand and Georgi.[22] Figure 35A shows localized areas of greater swelling where the reaction has started. Figure 35B shows small beads of lye exuding from the surface of the fiber which has become hydrophobic due to the introduction of benzyl groups. The progress of the reaction can be followed by the continuing separation of lye droplets which collect in the spaces between the growth rings and in the lumen of the cotton fibers. The sectional views in Figures 35D and 35E show the migration of droplets of dilute caustic and salt solution from the organophilic outer layers to the fiber core, these droplets depositing in the longitudinal channels between the growth rings. Figure 35F shows a more advanced stage in the reaction. The outer layer of gelatinous material has about 50% of its available hydroxyl etherified and is swollen but not dissolved in benzyl chloride. At this stage, the reaction stops because no more alkali is available.

To increase the substitution, the jelly must be broken up by vigorous agitation with fresh alkali (30% or higher). After a further slight increase in substitution, the jelly dissolves in benzyl chloride and the fibers progress toward complete dispersion[22] (Fig. 35C).

These pictures of the benzylation process show that the reaction proceeds from layer to layer and is conditioned by the difficulty of diffusion of benzyl chloride into the fiber. The speed of diffusion governs the advance of the reaction zone from layer to layer in the microstructure and presumably from layers of chains throughout the crystallites. When this speed of propagation of the reaction zone is about equal to the rate of benzylation of the individual hydroxyls, diffusion and reaction go hand in hand and the uniformity of substitution throughout the fiber reaches the maximum that can be expected for this type of heterogeneous reaction.

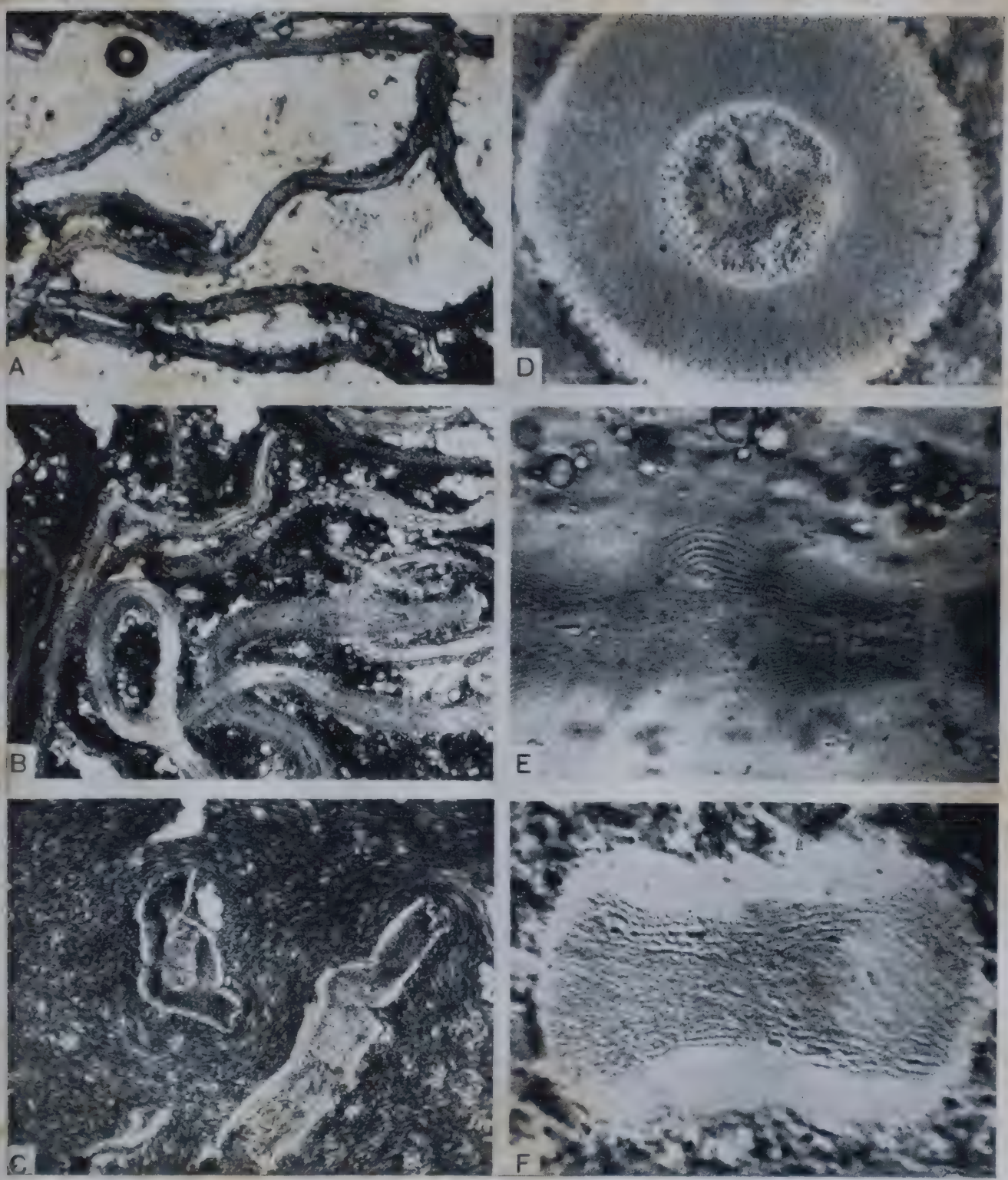

FIG. 35.—BENZYLATION OF CELLULOSE (LORAND AND GEORGI[22]).

A and B—Fibers at early stages of benzylation.

C—Benzylated fibers breaking up as gel sheath dissolves.

D and E—Sections through benzylated fiber at an advanced stage of benzylation

F—Section through benzylated fiber showing gelatinization of outer layers.

Magnification for A, B, and C: × 90.

Magnification for D, E, and F: × 350.

When the rate of benzylation exceeds the speed of advance of the reaction zone, the outer layers take up more benzyl groups, and these hydrophobic layers expel lye droplets to the interior of the fiber, diluting the caustic there. The highly benzylated outer layers also swell with the benzyl chloride and form a jelly which prevents introduction of fresh alkali into the less benzylated fiber interior. Less uniformly substituted ethers result which are undesirable from a technical standpoint since they also are nonuniform in their behavior in solution or on colloiding to form plastics.

Heterogeneity Due to Lyophilic Swelling Agent and Lyophobic Reaction Product. The benzylation of cellulose, because of the highly hydrophobic character of the etherifying group, is an extreme example of a type of physicochemical heterogeneity which most etherifications of cellulose have in common. The more hydroxyls which are etherified in a given layer in the fine structure of the cellulose fiber, the less capable it becomes of being swelled by the base or of further etherification.

This condition is in marked contrast to the acetylation of cellulose, for example, where the reaction is favored by the fact that the more hydroxyls which are acetylated, the more soluble the product becomes in the reaction mixture. In other words, when a lyophilic swelling agent produces a lyophilic reaction product, it is not difficult to reach practically complete trisubstitution of cellulose.

It has been proposed to prepare completely trimethylated celluloses by reacting cellulose acetate in acetone with aqueous caustic and dimethyl sulfate.[16, 55, 56] Recently, Johnston[53] showed that even this reaction was not homogeneous. When concentrated sodium hydroxide solution and dimethyl sulfate were added, the latter dissolved but the caustic solution formed small globules. Reaction occurred at the interface of these droplets with the solution and encased them in a thin sheath of methylcellulose film. After a time, the globules disappeared and were followed by a dispersion of methylcellulose in finely divided form. The experiments showed that the benefits expected from a reaction in a homogeneous system were not realized because the main reaction occurred on the precipitate. After D.S. 2.9 to 2.95 was reached, the reaction rate slowed down without attaining completely the theoretical D.S. 3.0.[37]

Attempts to methylate cellulose completely by reaction of its solution in benzyltrimethylammonium hydroxide showed a limit of substitution at D.S. 2.82. Although the reaction was homogeneous up to about D.S. 2.0,

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[55] E. Heuser and N. Hiemer, *Cellulosechem.*, **6**, 101, 125 (1925).

[56] W. N. Haworth and H. Machemer, *J. Chem. Soc.*, **1932**, 2276.

further methylation took place on a suspension of methylated cellulose. Both the above methylations illustrate the transition from a quasi-homogeneous reaction to a heterogeneous one due to transition of lyophilic cellulose to lyophobic derivative,[53] although the reaction is not complicated by the morphology of the cellulose fiber as in the case of benzylation reported by Lorand and Georgi.[22]

Heterogeneous Micellar Reaction. In aqueous sodium hydroxide, there is considerable evidence from the uniformity of solubility properties of the product that the course of etherification is influenced by the range of NaOH concentration used to swell the cellulose. This not only determines the proportion of NaOH and H_2O absorbed by the fiber but also the spacings of the alkali cellulose lattice (see Section D of this chapter).

Industrial studies of the production of alkali-soluble and water-soluble methyl, ethyl, and hydroxyethyl ethers indicate that products which are more smoothly dispersible and more easily filtered are obtained from cellulose swollen in 25–40% NaOH than in lower strengths, for example, 10–20% NaOH, even though the average degrees of substitution as indicated by analysis may be the same on ethers prepared in both ranges of NaOH concentrations. One factor influencing this behavior is undoubtedly the competition of NaOH associated with cellulosic hydroxyls and of NaOH associated with water for reaction with the etherifying agent.

In Section D of this chapter on alkali cellulose, it has been shown that water absorption is very large between 10 and 20% NaOH. It reaches a maximum at about 14% NaOH, decreases rapidly with increasing NaOH concentration, and tends to reach a more or less level minimum above about 30% NaOH (see Figs. 16 and 17 in Section D of this chapter).

The second factor influencing the uniformity of etherification appears to be the type of alkali cellulose produced by intermicellar swelling. X-ray evidence indicates no change in spacing between the chains in the crystallites up to about 12% NaOH. Between 12 and 18% NaOH, a definite change in crystal structure occurs which is considered generally to be due to formation of a hydrate of the compound $(C_6H_{10}O_5)_2 \cdot NaOH$. This has been referred to as soda cellulose I and is considered to be structurally related to cellulose hydrate. Between 20 and 40% NaOH, a second modification of the crystallite appears to exist. This has been called soda cellulose II and is related in its structure to the original cellulose.[47] The swelling compound with the crystallites is thought to contain one NaOH per glucose unit. Other modifications, probably due to various degrees of hydration, have also been reported (see Section D of this chapter).

3. Hemimethylcellulose

On methylating a suspension of ramie fibers in 11% NaOH and in 18% NaOH with dimethyl sulfate, Hess and Trogus[47] found that the methylated fibers showed the pattern of hydrate cellulose mixed with the pattern of trimethylcellulose as high as about D.S. 1.6. When 45% NaOH was used, however, the pattern of hydrate cellulose gave way at D.S. 0.65 to a new pattern, which corresponded neither to hydrate nor to trimethylcellulose. On further investigation, this pattern was found to correspond to one CH_3 group for each C_{12} unit and to appear at D.S. 0.5 in methylations of ramie suspended in 25 to 45% NaOH.[25] This pattern was mixed with that of trimethylcellulose up to about D.S. 1.5, when it no longer appeared.

Fibers of soda cellulose II were removed from the 30% NaOH solution, washed with 18% NaOH in methyl alcohol, and blotted dry. On immediate immersion in dimethyl sulfate, a vigorous reaction ensued which was complete in about 10 minutes. The fibrous product varied between D.S. 0.5 and 0.6, gave characteristic x-ray patterns in both anhydrous and hydrated condition, and was swelled to 8 to 10 times its volume with water. On drying, the swelled fibers became horny (a characteristic of highly hydrated methylated cellulose fibers). Hess and coworkers did not examine this product for solubility in 4–8% NaOH but it should be readily swollen and dispersed in this solvent, probably without necessity for freezing.

The amount of methanol (and associated NaOH) left after blotting to solvate the soda cellulose II was reported to be very critical. Too much gave incomplete methylation to the hemimethyl stage, too little resulted in extensive formation of trimethylcellulose as shown both by x-ray patterns and by extraction with chloroform. Washing with ether also gave this result, indicating that chloroform and ether are poorer solvating agents than methanol for soda cellulose II.

The hydrolytic products of soda cellulose II fibers, methylated after washing with 18% methyl alcoholic NaOH and blotting to the proper methanol content, were determined. The percentage of unmethylated glucose found was plotted against the methoxyl content of the fibers in curve II of Figure 36.

The corresponding values obtained from methylated similarly-dehydrated soda cellulose II, but with which an ether wash had been used, are shown in curve I. The theoretical curves, obtained by assuming that all of the substituting methyl groups go entirely to mono-, di-, or tri-methylate the individual glucose units, are also shown in Figure 36. Comparison of curves I

and II with the calculated curves further substantiates the position taken by Spurlin[46] that substitution is entirely random. The percentages of mono-, di-, and tri-substituted, and unsubstituted residues of curve II fit most closely the curve of Figure 34 for reaction rates of 1 : 1 : 10 for the 2, 3, and 6 OH groups, while the values of curve I of Figure 36 fit those calculated by Spurlin for 1 : 1 : 1 ratios of reactivities of these glucose hydroxyls. This agreement with the 1 : 1 : 10 ratio of reaction rates is

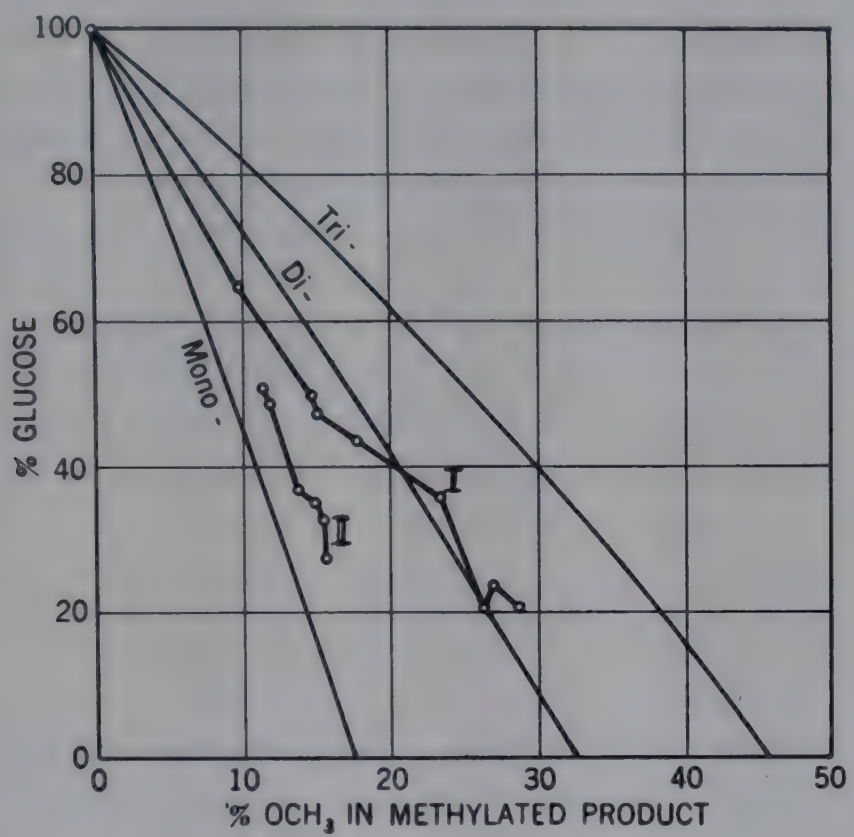

FIG. 36.—DISTRIBUTION OF METHOXYL GROUPS ON HEMIMETHYLCELLULOSE (HESS, TROGUS, EVEKING, AND GARTHE[25]).

Curves:

I, from ether-washed soda cellulose II.

II, from soda cellulose II after washing with NaOH in methanol.

about that obtained for quasi-homogeneous etherifications such as the preparation of water-soluble methylcelluloses from sodium cupricellulose.[46] The agreement of curve I with the distribution calculated from 1 : 1 : 1 reaction rates is about that found in more heterogeneous reactions such as the reaction of methyl chloride and alkali cellulose to water-soluble products.

Hemimethylcelluloses have also been prepared with good uniformity from sodium cupricellulose.[36, 38, 40] Cellulose is mixed intimately with one mole of $CuCl_2$ for each C_{12} unit and impregnated with a large excess of 15–16% NaOH. The $Cu(OH)_2$ first formed is taken up by the fibers in a

deep blue swelling complex with the NaOH. This product is worked and allowed to stand several hours, after which the excess NaOH is pressed out. It is then suspended in a large volume of water containing 5 moles NaOH per mole of Na_2CuC_{12} unit to prevent hydrolysis to free $Cu(OH)_2$. Methylation is effected with $(CH_3)_2SO_4$ at room temperature using agitation.[38]

When the methylation is conducted with methyl chloride, the sodium cupricellulose is pressed to a NaOH : cellulose ratio of 4, keeping $Cu(OH)_2$: cellulose equal to 0.5, and the press cake is then treated with methyl chloride vapors.[36, 38] Hemimethylcelluloses of D.S. 0.46 to 0.5 were hydrolyzed and the presence of 3-methylglucose was considered proved by the formation of an osazone with phenylhydrazine.[39] Other methylated products were present but not identified. On acetolysis, considerable quantities of cellobiose octaacetate were obtained but no dimethyl-

TABLE 3

DISTRIBUTION OF METHYL GROUPS IN HEMIMETHYLCELLULOSE

Substituents per glucose unit	Found[40]	Calculated[a, 46]
0	53.8	54
1	38.9	42
2	7.3	4

[a] Calculated for ratios of reaction rate constants of 2, 3, and 6 OH of 1 : 1 : 10, respectively.

cellobiose hexaacetate could be found.[40] The average uniformity of substitution of this product is almost theoretical. This is indicated by the comparison in Table 3 of the distribution of methyl groups found[40] with that calculated by Spurlin.[46]

A hemiethylcellulose prepared by treating sodium cupricellulose with ethyl chloride was reported to have a D.S. of 0.5. It was largely soluble in cold and hot water and swelled extensively in pyridine or cuprammonium, in which it formed solutions. Methyl alcoholysis results indicated that this product was entirely random in substitution.

A commercial methylcellulose prepared by this process was found to have a D.S. of 0.1 and to be readily soluble in 4% NaOH without freezing. On heating a 5% solution in 4% NaOH, gelation occurred at 37°C. and precipitation was complete at 45°C.[11] Presumably, methylcelluloses of D.S. 0.5 would also dissolve readily in 4–6% NaOH, but solutions should not gel on heating.

Another interesting preparation of hemimethylcellulose is that of Lieser,[57]

[57] T. Lieser, *Ann.*, **470**, 104 (1929).

who isolated and purified fibrous cellulose dithiocarbonate and then reacted it in alkaline methanol suspension with (nitroso)methylurethan. The latter, in the presence of the alkali, hydrolyzed to give the diazotate of nitromethane (equations (5) and (6)).

$$CH_3—\underset{\underset{NO}{|}}{N}—COOC_2H_5 + 2KOH \rightarrow CH_3N{=}NOK + C_2H_5OH + KHCO_3 \qquad (5)$$

$$(C_{12}H_{19}O_9—OCSSNa)_x + CH_3N{=}NOK \rightarrow (C_{12}H_{19}O_9OCH_3)_x + COS + N_2 + KNaS \qquad (6)$$

Lieser reported that this product had a D.S. of 0.3 to 0.35 and swelled in mercerizing strength NaOH without dissolving. Its solubility in 4–8% NaOH was not tested but it should have been readily dispersible. On acetolysis, cellobiose octaacetate was obtained, which showed again the randomness of substitution of the original dithiocarbonate group.[58] On methanolysis, a mixture of about equal parts of glucose and methylglucoses was obtained from which, after removing the glucose by fermentation, 2-methylglucose was identified as the phenylhydrazone.[57]

Lieser[37] considered all three hemimethylcelluloses prepared by widely varying processes to be identical in the respect that they are all examples of micellar-heterogeneous surface reactions. He inferred that, from their methods of preparation, the so-called hemimethylcelluloses resulted from methylations on anhydroglucose chains on the micellar surfaces. Since the proportion of chains on the surface to those on the interior of the micelles is slightly more than 1 : 1, the analytical values for one methyl per C_{12} are probably fortuitous. Lieser found no satisfactory explanation for the fact that in these, and analogous cases reported by Andress,[59] approximately 2 $C_6H_{10}O_5$ groups react as a unit. Neither did Hess and coworkers discuss any reason for the apparent crystallinity of the hemimethylcellulose they prepared from soda cellulose II. The whole picture presented by the hemimethylcelluloses suggests the possibility that the methylcelluloses of low substitution will be the means to unlocking the secrets of the fine structure of the organization of cellulose.

4. Alkali-Soluble Cellulose Ethers

In the preceding discussion of the heterogeneous nature of etherifications on cellulose fibers, it has been shown that, during the over-all interaction of etherifying agents and the swelling compound of cellulose with aqueous bases, there is a gradual transition from lyophilic cellulose to lyophobic

[58] T. Lieser, *Ann.*, **483,** 132 (1930).

[59] K. R. Andress, *Z. physik. Chem.*, **136,** 279 (1928); **A151,** 425 (1930).

cellulose.[22] This transition proceeds from layer to layer throughout the fine structure of cellulose and from the more easily accessible cellulose chains in the amorphous regions to the less readily etherified chains in the crystallites.[28, 34]

However, with the proper choice of etherifying agents, alkali cellulose composition, and reaction conditions, cellulose can be etherified so that all portions of the fiber remain more or less uniformly hydrophilic as evidenced by their solubility behavior in dilute aqueous sodium hydroxide. Methyl, ethyl, hydroxyethyl (glycol), or carboxymethyl (glycolic acid) groups are introduced by reacting upon cellulose swollen in caustic soda of not more than 50% concentration to form lower ethers of cellulose generally containing from 0.1 to 0.5 groups per glucose unit. Like cellulose, they are insoluble in water, soluble in cuprammonium, and are swelled by dilute alkalies. The concentration range at which they show maximum swelling, however, is much lower, namely, 4–8%, and this swelling can result in complete dispersion to viscous solutions with concentrations of cellulose ether less than about 10%.

In general, these ethers of low substitution show two types of solubility depending both upon the uniformity and the degree of substitution: (1) Swelled by 4–10% NaOH; dispersible to smooth solutions only at low temperatures (0°C. to the freezing point of the caustic solution employed); (2) Swelled by water; dispersible in 4–10% NaOH to smooth solutions at room temperatures (0 to 25°C.). An ether of a given degree of substitution may exhibit either of the solubility behaviors in 4–10% NaOH depending upon the extent of degradation of the cellulose from which it is made. Ethers of highly degraded celluloses will not be considered here since the principal technical interest is reported to be in those products prepared from purified cotton linters or high alpha-cellulose pulp.

These ethers of low substitution have been the subject of intensive industrial study in recent years with a view toward finding a more economical method of preparing regenerated cellulosic films and filaments of improved properties over those obtained by the viscose process.

(*a*) *Methylcelluloses and Ethylcelluloses*

In the preparation of methyl or ethyl ethers of D.S. 0.1 to 0.35, high alpha-cellulose is converted to alkali cellulose by steeping in 15–25% NaOH, pressing, and shredding to crumbs in the same manner as for viscose.[60]

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[60] D. C. Ellsworth and F. C. Hahn (to E. I. du Pont de Nemours & Co.), U. S. Patents 2,157,530 (May 9, 1939); 2,249,754 (Jan. 22, 1941).

After suitable aging, it is reacted at below 0°C. with methyl or ethyl sulfate, preferably diluted with ether, until the desired substitution has been reached. The reaction can be stopped by drowning in 2% sulfuric acid. The product (D.S. 0.15–0.20) dissolves in 10% NaOH on freezing and at ordinary temperatures in solutions of cuprammonium, calcium thiocyanate or zinc chloride. Although these ethers are hygroscopic, they give dry films of high tensile strength and may possibly replace viscose films.[1]

The etherified reaction product can also be used without isolation to prepare films, filaments, or paper sizing solutions by suspending it in a large excess of 6% NaOH and cooling with mechanical mixing below 0°C. until the mass freezes. This produces a smooth dispersion which may be kept at room temperature but gels on long standing or on raising the temperature. The gelled mass is readily liquefied again by chilling. This reversible sol-gel transformation undoubtedly follows the same mechanism as the more highly methylated water-soluble methylcellulose (see p. 791). Solution occurs due to hydration of the unetherified hydroxyl groups, a process which is favored by low temperatures. Gelation occurs due to partial dehydration of the hydrated envelope.

The solutions so prepared are readily filtered. On regeneration with dilute acids or with sodium sulfate solution, coagulation is said to occur more readily than with viscose, yielding a wet film of higher gel strength and a dried film of greater resistance to deformation. Moistureproofing coatings can be anchored to these etherified films much more firmly than to cellulose regenerated from viscose.[52]

In order to produce smooth solutions, each alkali-swollen fiber must receive a minimum of etherifying agent. To insure uniform distribution of the small amounts required and to prevent local over-etherification, cellulose may be impregnated with an aqueous solution of the etherifying agent, for example, sodium methyl sulfate, glycerol chlorohydrin, or sodium chloroacetate. The excess is pressed out, the impregnated cellulose is shredded, and then reacted upon with aqueous alkali (30–50% NaOH).[61] This principle of using water-soluble etherifying agents can be applied also to the continuous preparation of such low-substituted ethers.[23]

Freezing also produces smooth dispersions of low-substituted alkyl ethers of cellulose which are prepared under conditions such that the etherification is not entirely uniform throughout the fiber. For example, Denham and Woodhouse[9] reacted purified cellulose, swollen in three to four times its weight of 15–17% NaOH, with an amount of dimethyl sulfate

[61] J. F. Haskins and R. W. Maxwell (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,131,733 (Oct. 4, 1938).

equivalent to the alkali present. No cooling or mechanical agitation was employed. Methylation occurred with evolution of heat, and the alkali was not completely utilized.

The products of one such methylation of cotton wool or "normal" cellulose were dried and found to contain 0.44 to 0.54 methyl groups per glucose unit. Denham and Woodhouse reported these materials to be only slightly dissolved in 15% NaOH.[9] It can be shown easily that methylcelluloses of D.S. 0.4, 0.5, or 0.75 prepared by their directions are highly swollen in 8% NaOH at ordinary temperatures and readily yield smooth flowable dispersions after freezing.[44]

The swelling and dispersing power of 5–10% NaOH solutions for the low-substituted alkyl cellulose ethers was not generally recognized, however, until several years later when Lilienfeld pointed it out in a patent claim to alkali-soluble cellulose ethers.[62] Cellulose swollen in 12–25% NaOH was treated with methyl or ethyl chloride in amount insufficient to neutralize more than three-fourths of the NaOH present. Although the products are said to be dispersible in alkalies of 5–10% strength[62] and to be useful starting materials for preparing organo-soluble ethers,[63] most of the examples use regenerated cellulose.

(*b*) *Hydroxyalkyl Ethers*

The alkali-soluble hydroxyethyl ethers of cellulose were among the earliest materials considered with a view to preparing regenerated cellulosic films.[1] They have received considerable industrial attention for this use[64]

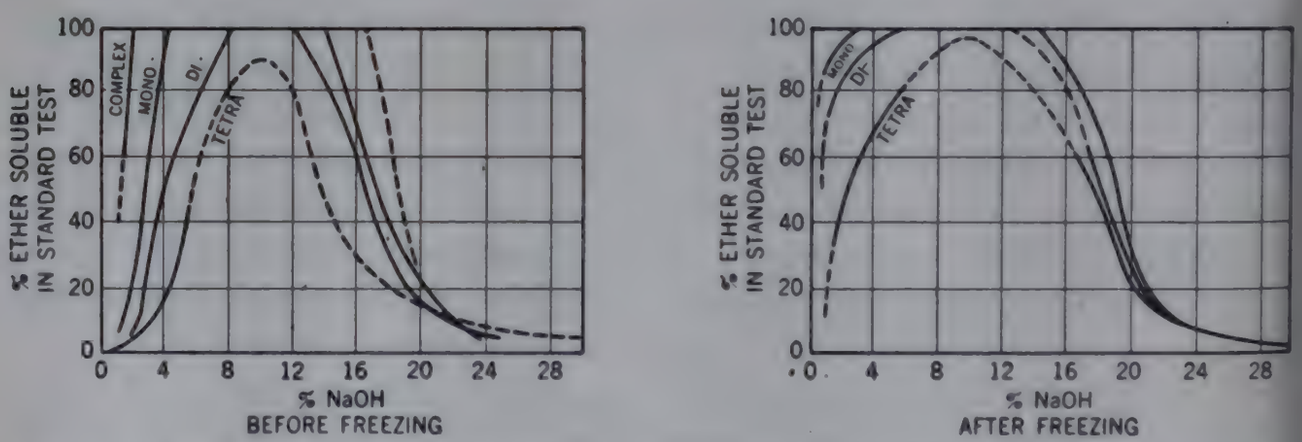

FIG. 37.—SOLUBILITY OF HYDROXYETHYL ETHERS OF CELLULOSE IN CAUSTIC SOLUTIONS (SCHORGER[64]).

[62] L. Lilienfeld, U. S. Patent 1,589,606 (June 22, 1926).

[63] L. Lilienfeld, U. S. Patent 1,589,607 (June 22, 1926).

[64] A. W. Schorger (to Burgess Laboratories), U. S. Patents 1,863,208 (June 14, 1932); 1,914,172 (June 13, 1933); 1,941,276–8 (Dec. 26, 1933).

as well as for permanent sizings for paper and textiles. Although the alkali-soluble hydroxyalkylcelluloses are said to range from a D.S. of 0.5 to 1.5,[1] the most useful materials are those having a D.S. of about 0.5 because the higher-substituted products tend to lose strength in water or even to become slimy.[65]

The preparation and properties of the alkali-soluble hydroxyethylcelluloses have been studied in detail by Schorger.[64, 65] Cellulose is steeped in 25% to 50% NaOH, preferably in 30% NaOH, from which it is pressed to a NaOH:cellulose ratio of 0.9 and a H_2O:cellulose ratio of 1.5. It is then etherified with good mixing by the action of sufficient ethylene chlorohydrin or ethylene oxide to introduce the desired amount of hydroxyethyl groups per glucose unit. The solubility of hydroxyethylcelluloses of D.S. 0.25 to 2.5 in aqueous NaOH is shown by the curves of Figure 37 for solutions at room temperature and for the solutions which have been frozen. The improvement in solubility is most marked at higher concentrations of the ether in 8% NaOH as shown in Figure 38. Maximum improvement in filterability of the solutions is obtained on freezing in 5–6% NaOH. It appears that freezing peptizes the less etherified fibers, since the fibrils could be seen unwinding and dispersing in the caustic during thawing.[65]

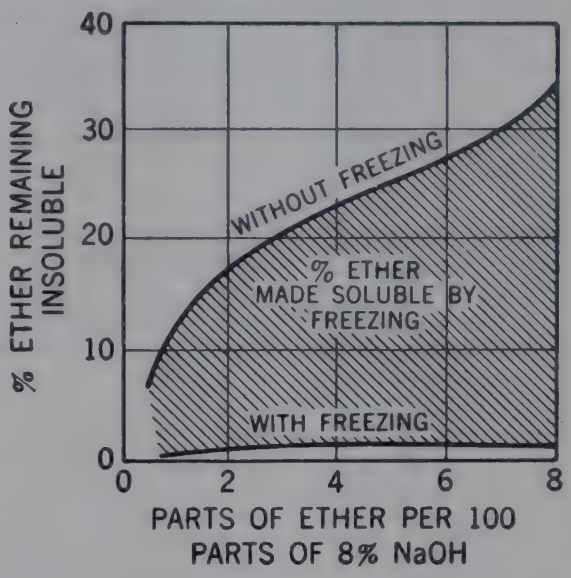

FIG. 38.—EFFECT OF FREEZING ON SOLUBILITY OF HYDROXYETHYLCELLULOSE IN 8% NaOH (SCHORGER[64]).

A more economical process recently reported forms alkali cellulose by treating a high alpha-cellulose pulp with 18% NaOH in the same manner as for viscose. After pressing and shredding, the crumbs are treated with an excess of ethylene chlorohydrin or of ethylene oxide until a D.S. of 0.3 is reached; the excess etherifying agent is used up by adding scrap viscose sheet or other regenerated cellulose. The mixed product has an average D.S. of 0.3 and is soluble in 10% NaOH at 0°C. but insoluble in water on regeneration with acidic solutions.[66]

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[65] A. W. Schorger and M. J. Shoemaker, *Ind. Eng. Chem.*, **29**, 114 (1937).

[66] F. H. Reichel and W. F. Hindry (to Sylvania Industrial Corp.), U. S. Patent 2,172,109 (Sept. 5, 1939).

(c) *Carboxymethylcellulose*

The ethers of cellulose resulting from the interaction of salts of chloroacetic acid with alkali cellulose form an interesting type of alkali-soluble cellulose derivative. The substituent carboxymethyl groups not only serve to space the chains apart and permit solvation of unsubstituted hydroxyls, but also are themselves salt-forming. In spite of this added solubilizing tendency, the solubility properties and industrial uses depend to a large extent upon the degree and uniformity of substitution.

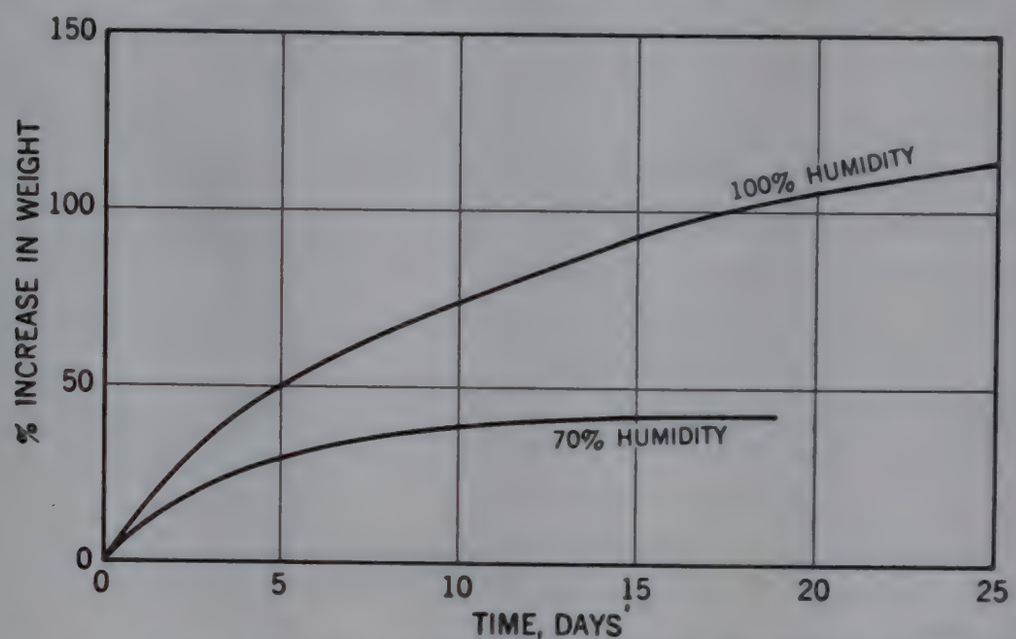

FIG. 39.—SODIUM CARBOXYMETHYLCELLULOSE: INCREASE IN WEIGHT DUE TO ITS HYGROSCOPICITY (BROWN AND HOUGHTON[69]).

Carboxymethylcellulose was first described in 1921,[67] and a product of D.S. 0.5 was evidently in commercial production in Germany prior to 1924.[68] It is present as the sodium salt in the reaction product of sodium chloroacetate on mercerized cellulose. The reaction mixture is soluble in water, both hot and cold, and the sodium salt can be isolated, after neutralizing the excess alkali, by precipitation with alcohol.

The sodium salt is a white fluffy solid which is highly hygroscopic as the curves of Figure 39 show. It forms smooth viscous solutions in water from which insoluble salts of aluminum, lead, copper, zinc, and silver can be prepared.[67, 68] On evaporation, solutions of the sodium salt yield clear tough films which are highly hygroscopic.[68, 69]

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[67] E. Jansen (to Deutsche Celluloid Fabrik, Eilenburg), German Patent 332,203 (Jan. 22, 1921).

[68] J. K. Chowdhury, *Biochem. Z.*, **148**, 76 (1924).

[69] C. J. Brown and A. A. Houghton, *J. Soc. Chem. Ind.*, **60**, 254T (1941).

When caustic of 30–50% strength is used to impregnate the cellulose, the resulting alkali-soluble carboxymethyl ethers do not begin to precipitate until *p*H of 6.0. This is shown for D.S. 0.3 by the curves of Figure 40 which also represent the behavior of ethers of D.S. 0.5 to 0.8.[44] Carboxymethylcellulose is a moderately strong acid with a dissociation constant of about 5×10^{-5} and is not completely liberated from its sodium salt until the *p*H is reduced to 2.5.[69]

With carboxymethyl ethers of D.S. 0.3, the acid is precipitated from its sodium salt on acidification, but on long standing in water swells strongly

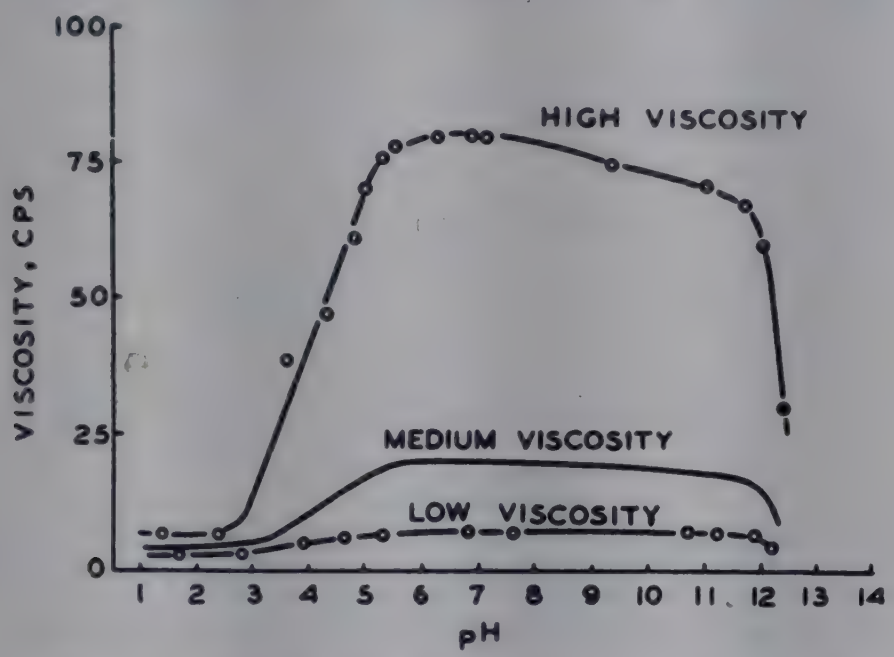

FIG. 40.—SODIUM CARBOXYMETHYLCELLULOSE: VARIATION OF VISCOSITY OF 1% AQUEOUS SOLUTIONS WITH *p*H AT CONSTANT TEMPERATURE (20°C.) (BROWN AND HOUGHTON[69]).

and eventually yields a transparent solution containing about 99% water.[69] With a D.S. of 0.5 to 0.8, the acid does not precipitate on acidification but can be thrown down with alcohol. While still wet, it is readily soluble in water, but, after drying, it is insoluble and can be redissolved only by dilute alkalies.[44, 68, 70] Chowdhury[68] attributed this behavior to dehydration on drying with the formation of an inner lactone.

Solutions of the sodium salt of carboxymethylcellulose of D.S. 0.3 decrease in viscosity with increasing *p*H as shown by the curves of Figure 40. This decrease is not due to degradation, since the viscosity regains its original value by reducing the *p*H to neutrality. One explanation offered

[70] I. Sakurada, *Z. angew. Chem.*, **42**, 640 (1929); W. R. Collings, R. D. Freeman, and R. C. Anthonisen (to Dow Chemical Co.), U. S. Patent 2,278,612 (Apr. 7, 1942).

is that the association of NaOH with unsubstituted hydroxyls breaks cross-linking bonds between hydroxyls of neighboring chains.[69]

Solutions of the sodium salt of carboxymethylcellulose of D.S. 0.3 do not gel on heating but do undergo a viscosity decrease. The curves of Figure 41 show that this change begins at about 50°C. for a 1% solution of a given viscosity type. The temperature undoubtedly is characteristic of the concentration and average molecular weight of the ether used, since a similar phenomenon occurs with water-soluble methylcellulose.[44]

The viscosity changes on heating solutions of sodium carboxymethylcellulose, unlike those of methylcellulose, are not completely reversible.

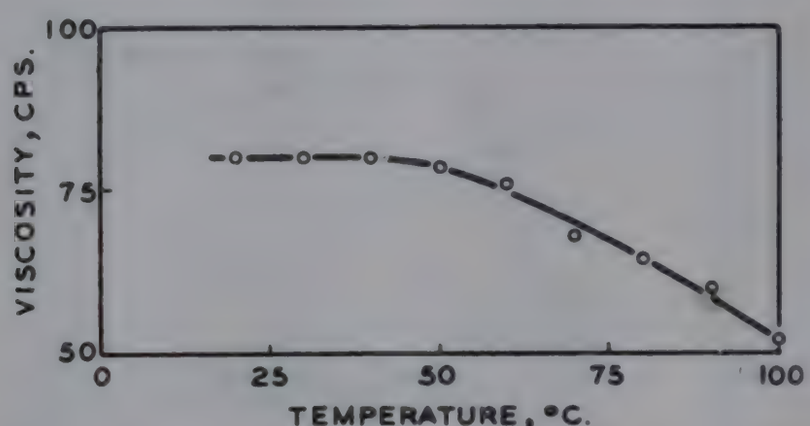

FIG. 41.—SODIUM CARBOXYMETHYLCELLULOSE: VARIATION OF VISCOSITY OF 1% AQUEOUS SOLUTIONS WITH TEMPERATURE OF HEATING (BROWN AND HOUGHTON[69]).

Viscosities were measured at 20°C. after heating to the temperatures indicated for 20 minutes.

The curves of Figure 42 show that the viscosity decrease on heating is not regained on cooling. This irreversibility has been suggested as being due to the breaking of cross linkages or hydroxyl bonds which are present in solutions of sodium carboxymethylcellulose which have been formed in cold water,[69] but is more probably due to a permanent partial dehydration of solvated molecules with heat. Apparently the dehydration of the solvated molecules present in sodium carboxymethylcellulose solutions on the addition of polyvalent negative ions is not as extensive as in the case of methylcellulose, since the solutions do not gel even when saturated salt solutions are added.

The insoluble salts of carboxymethylcellulose of D.S. 0.5 to 0.75 are swelled and dissolved by dilute aqueous ammonia, sodium hydroxide, and ethylenediamine. The solutions are stable to heat and are reduced in viscosity by higher content of base. The aluminum salt is easily prepared from a neutral filtered solution of the etherification mixture by running it

into an alum solution. This offers a convenient way of isolating a technically useful product, since solutions of the aluminum salt in dilute ammonia are useful thickeners and protective colloids.[44]

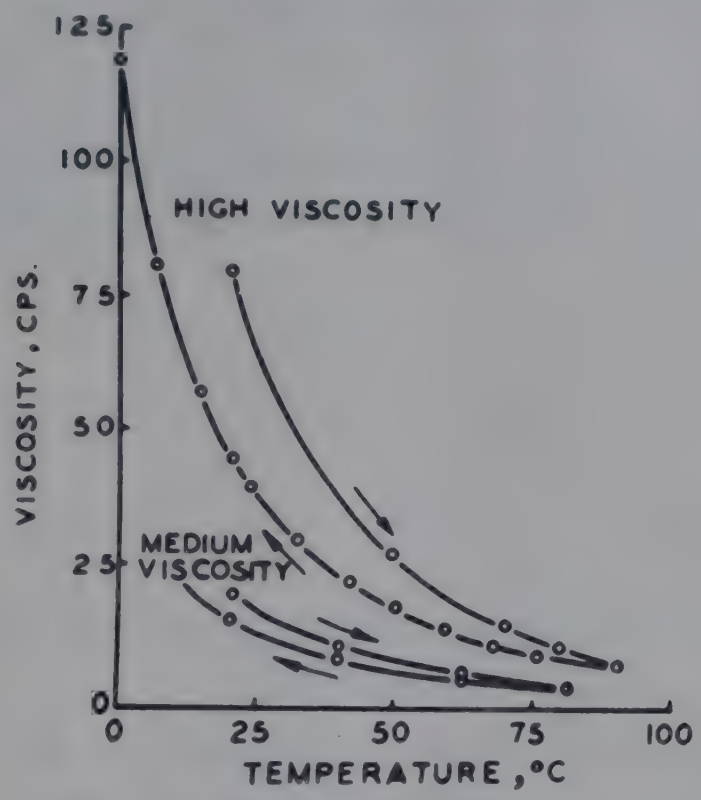

FIG. 42.—SODIUM CARBOXYMETHYLCELLULOSE: VARIATION OF VISCOSITY OF 1% AQUEOUS SOLUTIONS WITH TEMPERATURE OF MEASUREMENT AT CONSTANT *p*H (5.0) (BROWN AND HOUGHTON[69]).

5. Water-Soluble Cellulose Ethers

The principal water-soluble ethers of cellulose are methyl, ethyl, hydroxyethyl, and sodium carboxymethyl. They result from reacting the corresponding etherifying agents with the system: cellulose : base : water, using compositions such that the contained cellulose is at least highly swollen or, in some cases, completely dispersed in the aqueous base. The reaction generally stops when the etherified product becomes insoluble in the reaction mixture, when the base becomes too dilute, or when either the etherifying agent or the base is completely reacted.

Although sodium hydroxide has been the base most widely studied and industrially used, systems containing cellulose dispersed in other aqueous bases such as NaOH—$Cu(OH)_2$[35–40] or quaternary ammonium hydroxides[37, 42, 49, 50] have also been investigated. Cellulose is considered to be more homogeneously dispersed in these systems than in alkali cellulose

because the methylcelluloses or ethylcelluloses prepared from them exhibit water solubility at much lower average degrees of substitution.[42] Table 4 shows the degrees of substitution at which water solubility exists for the four principal water-soluble cellulose ethers.

TABLE 4

WATER SOLUBILITY OF CELLULOSE ETHERS AS A FUNCTION OF DEGREE OF SUBSTITUTION

Cellulose ether	Alkali cellulose D.S.	NaOH—$Cu(OH)_2$ cellulose, D.S.	Cellulose in quaternary base, D.S.
Methyl	1.3–2.6 (1.5–2.0)[9, 44, 71, 72, 73]	0.7–2.0[38, 40]	0.7–2.0[42]
Ethyl	0.8–1.3[54, 74]		
Hydroxyethyl	1.5–2.5[64, 65]		
Carboxymethyl (Na salt)	0.3–0.8[44]		

(a) *Effect of Uniformity of Substitution on Water Solubility of Methylcellulose*

Early attempts to produce methylcelluloses which were completely soluble in cold water were successful only when methylation conditions were so drastic as to degrade the product greatly[5, 7–10] or when the cellulose to be methylated was already degraded to the point of solubility in 15–18% NaOH.[71, 72] The failure to obtain water solubility on methylating purified cellulose seems to have been due to the use of 15% NaOH, which is a good swelling agent for cellulose but not strong enough to offset the rapid diluting effect resulting from the saponification of the dimethyl sulfate used. After five consecutive methylations, each with 2 moles of 15% NaOH and 1.5 times the amount of $(CH_3)_2SO_4$ calculated to react with the NaOH used, a product analyzing for dimethylcellulose was finally obtained. Neither this product nor that from any intermediate stage was more than partially soluble in water, as the data of Table 5 show.

Only after a sixth methylation, using 2 moles of 29% NaOH solution and 4 moles of $(CH_3)_2SO_4$, was any considerable degree of water solubility obtained. The practice of drying the product after each methylation undoubtedly helped retard the efficiency of the reaction, since the hard horny

[71] E. Heuser and W. von Neuenstein, *Cellulosechem.*, **3**, 89 (1922).
[72] E. Berl and H. Schupp, *Cellulosechem.*, **10**, 41 (1929).
[73] H. Staudinger and D. Schweitzer, *Ber.*, **63B**, 2327 (1930).
[74] E. J. Lorand, *Ind. Eng. Chem.*, **30**, 527 (1938).

urface of the product probably resisted the penetration of the caustic solu-ion.

On the other hand, little difficulty was reported in obtaining completely vater-soluble products from alkali-soluble forms of cellulose. Heuser and Neuenstein[71] methylated hydrocellulose dissolved in 15% NaOH and ob-tained a greater degree of substitution for each stage of methylation with the same conditions and reactant ratios which Denham and Woodhouse[9] used. Berl and Schupp[72] checked Lilienfeld's claim[7] that etherification of regenerated cellulose led to water-soluble products. The cellulose used

TABLE 5

METHYLATION OF COTTON CELLULOSE IN STAGES WITH 2 MOLES OF 15% NaOH AND EXCESS $(CH_3)_2SO_4$ (1.5 × THEORY) AT ROOM TEMPERATURE

No. of methyl-tions	Methoxyl content of product, %				% of product soluble in H_2O		% CH_3O in H_2O-soluble		Solubility in Cu-NH_3 reagent
	D + W[9]	D + W[10]	H + N[71]	B + S[72]	H + N[71]	B + S[72]	H + N[71]	B + S[72]	B + S[72]
1	10.1	5.3	10.5	17.4	0	13.5	..	17.4	100
2	16.8	11.5	21.7[a]	24.6	6[a]	15.5	32.6	..	69.5
3	22.1	14.0	25.8[a]	26.5	6[a]	14.0	30.5	..	53.1
4	..	18.7	26.2[a]	28.5	5.8	13.2	30.0	..	50.0
5	..	20.7	27.4[a]	31.6	18.5	11.8	29.4	32.0	12.1
6	..	23.9[b] 26.0	...	33.2	..	10.4	..	..[b]	10.7

[a] Estimated.

[b] Product of the fifth methylation treated with 2 moles of 29% by weight NaOH and 4 moles $(CH_3)_2SO_4$. Products combined and washed with water. Washings deposited gels on evaporation which redissolved on cooling. On further concentration, gels remained undissolved on cooling but redissolved as salts were removed by washing. The water-soluble portion analyzed 23.7% methoxyl (D.S. 1.4).

resulted from kneading cotton with 75% H_2SO_4 at −50°C. until it became fully soluble in alkalies and then washing free of acid with ice water. A single methylation of this cellulose, dissolved in 15% NaOH, gave 19–21% methoxyl content (D.S. 1.2), and three methylations in 30% NaOH gave a product of 30.7% methoxyl.

These methylated hydrocelluloses of approximately 1.2 to 2.0 methyl groups per glucose unit showed the same precipitation on heating their aqueous solutions as was reported by Denham and Woodhouse for their methylcellulose of D.S. 1.3. However, the product (D.S. 1.2) of Berl and Schupp did not form a gel until the solution was heated to its boiling point.

This product was precipitated by saturated NH_4NO_3 solution on heating, and the precipitate also redissolved on cooling. Saturated $Al_2(SO_4)_3$ solution precipitated the methylated hydrocellulose at ordinary temperatures and the gel would not redissolve until the salt had been washed out.

This property of precipitation on heating has also been shown by methylated products of related carbohydrates, starch, xylan, and lichenin.[71] Heuser and Neuenstein[71] recognized that the process of solution of dimethyl hydrocellulose in cold water and its precipitation on heating was due to a reversible hydration and dehydration of the dissolved molecules.

In recent years, improvements in the methylation of cellulose have led to the preparation of water-soluble methylcelluloses in a single-stage process. Higher concentrations of alkali were shown by Hess[75] to furnish the driving power required for higher methoxyl contents by preventing too much water absorption. The second step in improving the preparation of water-soluble methylcellulose was the use of methyl chloride instead of methyl sulfate.[8, 76, 77] This improved uniformity of substitution by virtue of greater diffusion into the alkali cellulose. It remained to select the proper composition ratios in the system cellulose : NaOH : H_2O which would most efficiently yield a uniformly methylated product of practically complete water solubility.[78]

(*b*) *The Sol-Gel Transformation of Methylcellulose Solutions on Heating*

It should be noted that all of the methylcelluloses prepared from alkali cellulose, regardless of the methoxyl content at which water solubility is obtained, are characterized by the fact that heating their solutions in cold water causes precipitation. The methoxyl content at which water solubility is obtained when other alkaline swelling agents are used and the behavior of the aqueous solutions of methylcelluloses produced from them will be discussed later.

The sol-gel transformation of methylcellulose solutions has been studied by Heymann.[79, 80] He called it an "inverse" transformation to contrast it with agar-agar and gelatin whose solutions gel on cooling. The change in solution viscosity with temperature, shown by curve I of Figure 43 for a 1.56% solution of a commercial methylcellulose of D.S. 2.14, is typical for

[75] K. Hess, G. Abel, W. Schon, and W. Komarewsky, *Cellulosechem.*, **16**, 69 (1935).
[76] G. Young, U. S. Patent 1,504,178 (Aug. 5, 1924).
[77] L. Lilienfeld, U. S. Patent 2,103,952 (Dec. 28, 1937).
[78] A. T. Maasberg (to Dow Chemical Co.), U. S. Patent 2,160,782 (May 30, 1939).
[79] E. Heymann, *Trans. Faraday Soc.*, **31**, 846 (1935).
[80] E. Heymann, *Trans. Faraday Soc.*, **32**, 462 (1936).

ll water-soluble ethers made by methylating alkali cellulose. The vis-
osity decreases with increasing temperature up to a temperature at which
ne direction of the curve changes, and small increments in temperature
roduce large rises in viscosity and eventually transform the solution into
jelly. This temperature decreases with increasing concentration of
nethylcellulose of a given average molecular weight or with increasing
nolecular weight at a given concentration. This is shown by the curves of

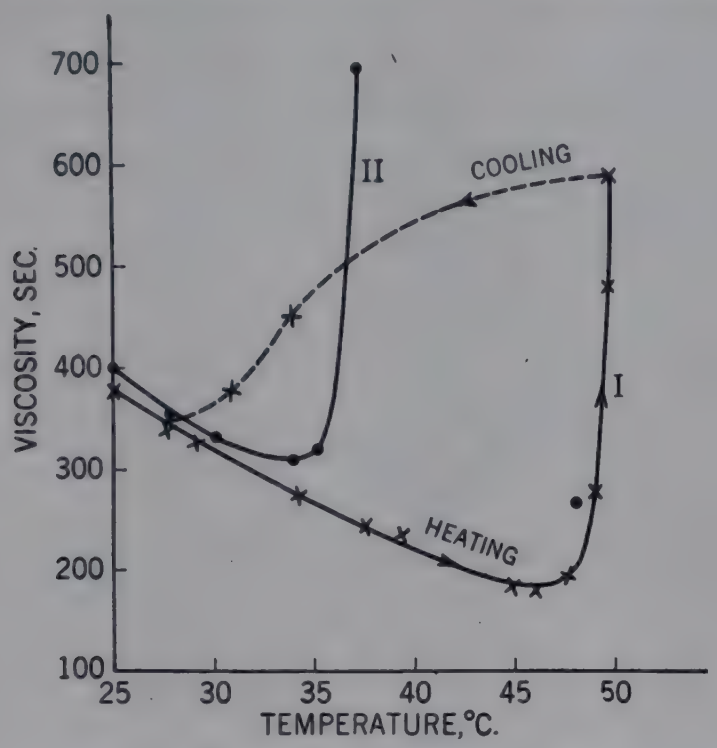

FIG. 43.—VISCOSITY CHANGES IN METHYLCELLULOSE SOLUTIONS ON HEATING; GEL FORMATION AND SYNERESIS (HEYMANN[79]).

Curves: I, methylcellulose (1.56% in water; D.S. 2.14); II, methylcellulose (1.52% in 0.1 *M* aqueous K_2SO_4).

Figure 44 for commercial methylcelluloses of D.S. 1.8 to 1.9.[81] When the gelled solution is cooled rapidly, the viscosity soon returns to its original value as shown in Figure 43, indicating that the sol-gel transformation is completely reversible.

The gelation temperature is strongly affected by the presence of small concentrations of soluble salts as curve II of Figure 43 shows. This effect resides almost entirely in the anions in the order of the well-known lyotropic series CNS > I > NO_3 > Br > Cl > acetate > tartrate > SO_4. Soluble thiocyanates and iodides raise the gelation temperature; the other anions decrease it.

Higher concentrations of the soluble salts flocculate methylcellulose from

[81] *Methocel.* The Dow Chemical Co., Midland, Mich., 1942.

solution, and the concentration of salt required decreases in the order of the lyotropic series. The influence of salts in small concentrations on the sol-gel transformation temperature and the amounts required to cause gelation at room temperature are quite parallel. Heymann concluded that the cause of both processes was the same, namely, dehydration of the methylcellulose "particles" in the solution.

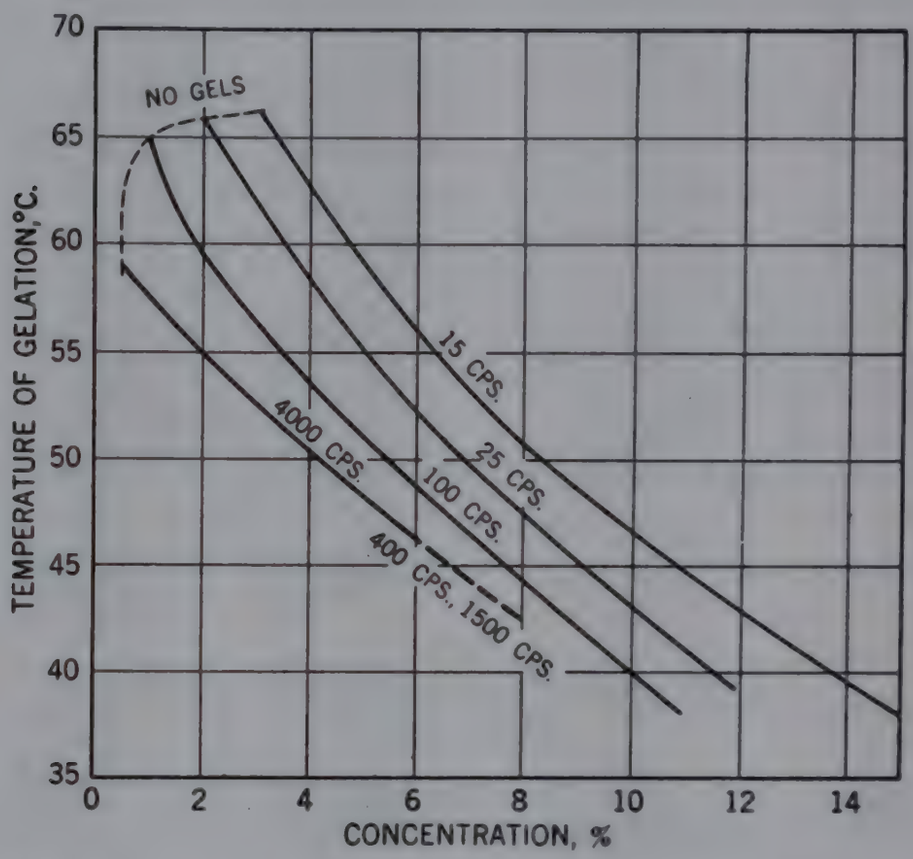

FIG. 44.—GELATION TEMPERATURE OF COMMERCIAL METHYLCELLULOSE (DOW CHEMICAL CO.[81]).

Viscosity types refer to absolute viscosity of 2% solutions in water at 25°C.

Heymann observed that methylcellulose sols tended to be thixotropic as the gelation temperature was approached. The viscosity of methylcellulose solutions showed only a small dependence upon pressure at lower temperatures, but became very much dependent on the shearing rate at temperatures nearing the gelation point. The steeply sloped curves A, B, and C of Figure 45 were considered to indicate that the gel structure, which was being built up in the sol, was increasingly broken down by the application of increasingly larger shear forces. Sulfate ions produced gel structure at a lower temperature and thiocyanate ions at a higher temperature than the salt-free solution.

Taking a more dilute solution in which the deviations from Poiseuille's law could be neglected, Heymann measured the change of the relative viscosity of the methylcellulose solution with temperature. The curve of Figure 46 shows a steady decline in the viscosity of the solution relative to that of water up to point A, about 10 degrees below the beginning of gelation. The curve then falls more steeply until at point B the usual increase due to gel formation sets in.

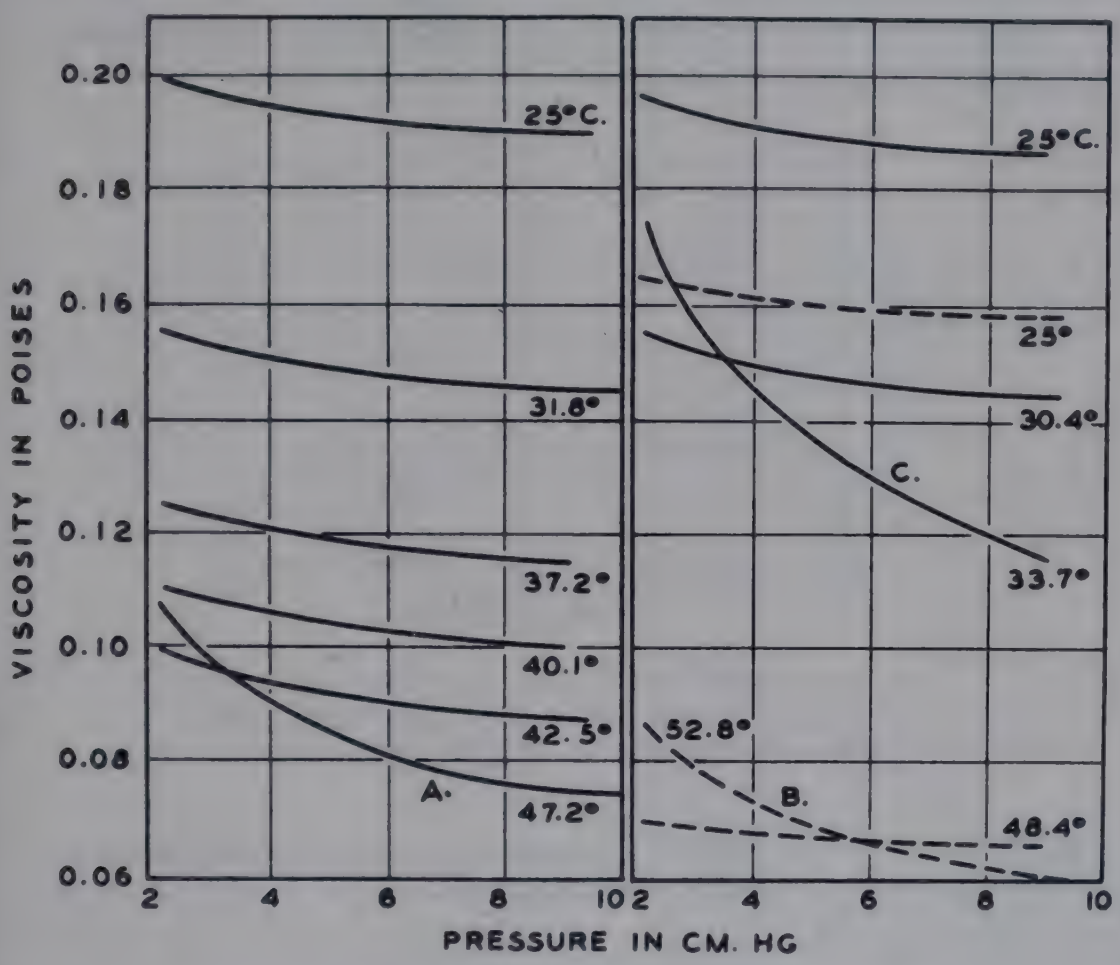

FIG. 45.—EFFECT OF RATE OF SHEAR IN METHYLCELLULOSE SOLUTIONS (1.72% IN WATER) AND IN 0.1 *M* AQUEOUS SALT SOLUTIONS (HEYMANN[79]).

Curves: A, in aqueous solutions; B, – – – –, in 0.1 *M* KCNS solution; C, ———, in 0.1 *M* K_2SO_4 solution.

The first portion of the curve shows the temperature coefficient of the solution to be greater than that of the solvent. Heymann attributed this to a decrease of hydration with rise in temperature or to the effective volume of the dissolved particle becoming smaller. This process accelerates as the temperature increases until the long particles interlace into large coagulates which may build up a loose network or gel. With short average chain lengths or at very low concentrations, the rapid decrease in relative vis-

cosity with temperature is accompanied by increasing turbidity until the solution suddenly becomes opalescent.[73] This is also shown by the region of "no gels" in Figure 44.

Conclusive evidence that the sol-gel transformation exhibited by methylcellulose solutions was due to changes in the degree of hydration was obtained by measuring the corresponding changes in volume.[79, 80] During gelation at constant temperature, a volume increase of 0.13 cc. per 100 g. of solid methylcellulose was observed. This was found to be only about 2% of the volume contraction which occurred when methylcellulose was originally dissolved in water, namely, 7 to 8 cc. per 100 g.

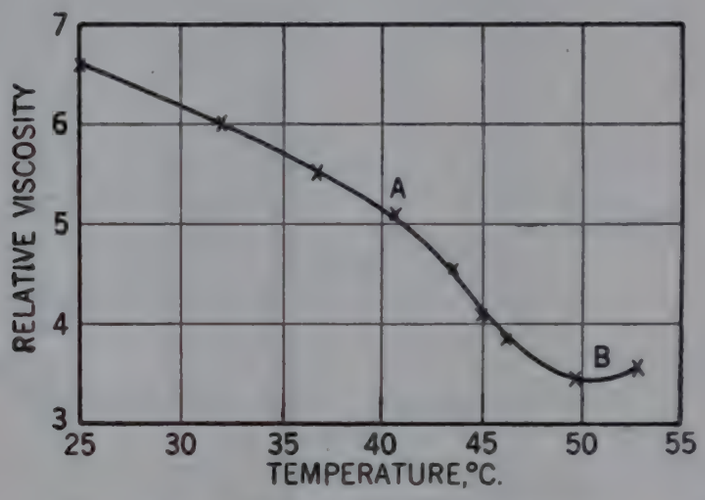

FIG. 46.—EFFECT OF TEMPERATURE ON RELATIVE VISCOSITY OF A METHYLCELLULOSE SOLUTION (0.965% IN WATER) (HEYMANN[79]).

Heymann pointed out that this large decrease in total volume on dissolving methylcellulose justified the conception that the water solvating the methylcellulose particles is bound by secondary forces. The water of the hydration layers has a smaller specific volume because it is compressed by the attractive forces between the water dipoles and the methylcellulose particles. The volume increase on sol-gel transformation is a result of the removal of part of the adsorbed water molecules and their consequent expansion to the original volume.

The above describes dehydration as a process in which the forces between the particles and the water molecules are broken by increasing the kinetic energy of the system, which releases water associated with the methylcellulose particles and decreases their effective volume in solution. This accounts both for the viscosity decrease with rise in temperature and for the observed volume increase on gelation. However, the mechanism is probably more complex, since dehydration and viscosity increases in

ıethylcellulose solutions are slow processes at temperatures not too far be-ow the gelation temperature. This is shown in the curves of Figure 47 by n initial decrease to a minimum viscosity followed by a continuous increase ue to progressive transformation to the gel. The initial viscosity drop is ccompanied by an initial increase in Tyndall intensity; the usual increase ue to gel formation becomes apparent only after a period of time.

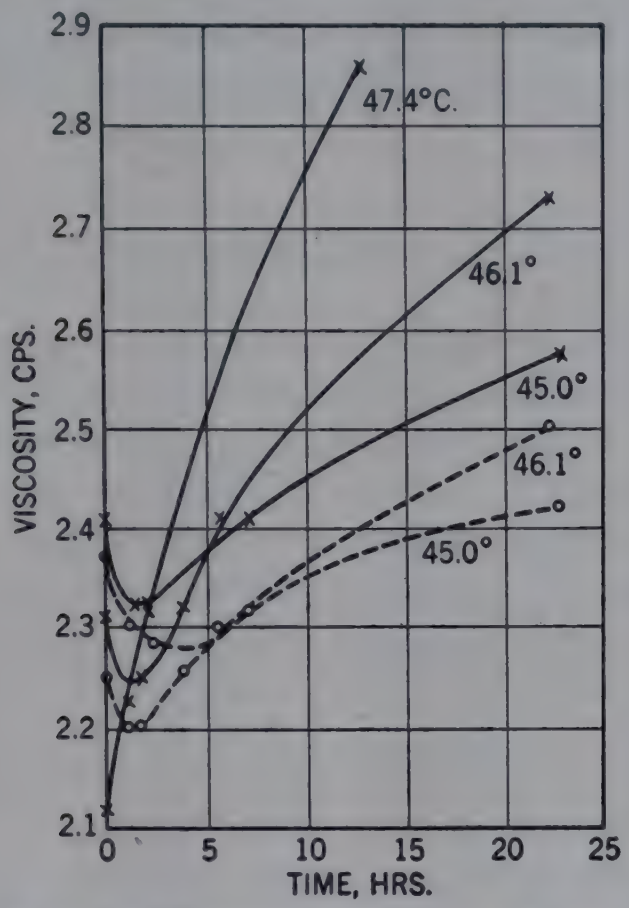

FIG. 47.—EFFECT OF TIME ON VISCOSITY OF A DILUTE SOLUTION OF METHYLCELLULOSE AS THE TEMPERATURE APPROACHES THE GELATION POINT OF THE SOLUTION (HEYMANN[79]).

——— Pressure = 2 cm. Hg.
– – – – Pressure = 4 cm. Hg.

The suggestions of Staudinger and Schweitzer[73] that the process is a decomposition of an oxonium hydroxide stable at low temperature cannot be the whole explanation, since the oxonium hydroxide must be hydrated. More probably, the hydrated particle cannot be quantitatively defined but is built up of water molecules adsorbed with decreasing bonding energy as the thickness of the hydration layer increases. This is in agreement with the observation of Katz[82] on cellulose that the differential heat of swelling

[82] J. R. Katz, J. C. Derkson, and W. F. Bon, *Rec. trav. chim.*, **50**, 725 (1931); **51**, 514 (1932).

decreases gradually with swelling. At low temperatures, there is n marked limit to the hydration layer but a more or less smooth transition t free water which does not preclude the possibility of immobilization o water layers by the shape effect of the methylcellulose particles. On heat ing, water molecules are sloughed off from the outer layer, decreasing th size of the hydrated particles while increasing their freedom of motion until a point is reached where the particles on dehydration come within each other's spheres of influence. Once coagulated, the gels knit together and on long aging, show marked syneresis and eventual crystallization in a macroscopic sense.[79, 80]

(c) *Water Solubility as a Function of Degree of Substitution*

The water solubility of cellulose ethers is generally considered to result from the fact that the individual cellulose chains are held apart by methoxyl or ethoxyl groups, making the remaining unetherified hydroxyl groups available for hydration.[42] This is in agreement with the postulate of Neale[83] that the swelling of cellulose in aqueous solution is a manifestation that hydroxyl groups are becoming more accessible for hydration. It is also in line with modern concepts that the fine structure of cellulose is a network of micelles oriented in the direction of the fiber axis and held together by secondary valence forces or hydrogen bridges.[30, 31] The alkali solution enters between the micelles, pushes the units apart, and loosens the interconnecting secondary bonds. While in this expanded condition methyl groups are distributed at random along the chains and serve as permanent wedges to keep them apart. The rupture of the secondary bonds is probably incomplete in the case of cellulose chains in the interior of the crystallites so the structure holds together at certain points. Hence to get smooth solutions, more methyl groups have to be introduced throughout the whole to insure complete separation of the less etherified portions of the chains by water. If too many methyl groups are introduced, however, the number of hydroxyl groups available for hydration is greatly reduced, and the product is incompletely soluble or only swelled by water.

To obtain water solubility in any given cellulose ether, therefore, a nice balance must be obtained between the kind, number, and distribution of the substituting radicals and the remaining unsubstituted hydroxyl groups. If an insufficient proportion of hydroxyls is substituted, the product may swell in water without dissolving. If too highly substituted, not enough

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[83] S. M. Neale, *J. Textile Inst.*, 15, T157 (1924).

TABLE 6

VARIATION OF SOLUBILITY OF CELLULOSE ETHERS WITH DEGREE OF SUBSTITUTION

Solubility stage	Methyl, D.S.		Ethyl, D.S.		Propyl, D.S.		Butyl, D.S.	
	A	B	A	B	A	B	A	B
1. Soluble in 4–8% NaOH on freezing	0.1[60]	..	..	..	..	..	..	..
	0.23–0.38[60]	..	..	..	..	..	..	..
2. Soluble in 4–8% NaOH	0.4–0.6[9, 54, 62, 74]	0.1[38]	0.5–0.7[54, 74]	..	..	..	..	..
3. Soluble in cold water	1.3–2.6[9, 44, 71, 72, 73]	1.1[38]	0.8–1.3[54, 74]	0.5[40]	..	..	..	..
				0.6[54]	..	..	..	..
4 Increasing swelling in (organic) polar-nonpolar solvent mixtures. Decreasing solubility in water. Increasing solubility in alcohol	2.0–2.6	..	1.4–1.8[72, 74]	1.0[40]	..	0.5[40]	..	..
5. Increasing solubility in the the above solvent mixtures. Decreasing swelling by water. Soluble in alcohol	2.6–	..	1.8–2.2[72, 74]	1.1–1.4[40]	1.5[44]	..	..	0.6–1.0[40]

Key: Column A: Data on materials prepared by alkylation of alkali cellulose.
Column B: Data on materials prepared by alkylation of sodium cupricellulose or of cellulose swelled with quaternary ammonium hydroxides.

hydroxyls remain available for hydration, and the product again is swelled without dissolving in water.

The relation between the degree of substitution of the lower alkyl ethers and their solubility in aqueous solutions is summarized in Table 6. The reported data indicate that the average number of methyl or ethyl groups per glucose unit which is required to make the ether soluble in water or in aqueous alkalies differs with the type of etherification reaction.

The table shows that higher degrees of substitution are required to obtain the desired solubility when the etherification is heterogeneous, as in the etherification of alkali cellulose, than when the reaction is quasi-homogeneous in type, as in the case of cellulose dispersed in a quaternary base or in the form of a copper-alkali cellulose complex.

The table also shows that, even with the most homogeneous types of etherification reported, water solubility is not obtained with the alkyl groups having more than two carbon atoms, probably due to their more hydrophobic character.

(*d*) *Cellulose Ethers Soluble in Hot and Cold Water*

In view of the difficulties experienced by early workers in obtaining completely water-soluble methylcelluloses from cellulose impregnated with 15–18% NaOH, it is particularly interesting to note the effect of adding $Cu(OH)_2$ to the system. Traube[38] impregnated cellulose with $CuSO_4$ or $CuCl_2$ until the Cu : C_{12} ratio was equal to one, and then treated with 16–18% NaOH. The $Cu(OH)_2$, first formed as the NaOH solution is imbibed into the fiber, combined with the cellulose in the presence of excess NaOH, and is reported to produce a completely homogeneous dispersion when viewed under the microscope.[36] Methylation to D.S. 0.9–1.1 or ethylation to D.S. 1.0–1.2 yields products which are completely soluble in cold water and form viscous solutions. The methylcellulose solutions do not gel on heating to boiling, and the ethylcellulose solutions do not separate until about 70°C. is reached.[38]

The fact that the solubility in cold water is obtained at degrees of substitution so much lower than those required for commercial methylcelluloses (or ethylcelluloses) was attributed to greater uniformity of alkylation. However, comparison of the yields of variously methylated glucoses reported with those calculated by Spurlin[46] indicates that the distribution of methyl groups was random and followed the laws of probability assuming equal availability of all OH groups for etherification.

Traube considered the hot-water solubility of the methylcelluloses pre-

red from sodium cupricellulose to be connected with the substantial ab-nce of trimethylated glucose units. This was confirmed by further ethylating hot-water-soluble methylcellulose of 15% methoxyl (D.S. 0.84) ith $(CH_3)_2SO_4$ in the presence of $Cu(OH)_2$ and NaOH to a product of .6% methoxyl (D.S. 2.15). This higher methylated product was fully luble in cold water but precipitated on heating. Separation of the ethyl glucosides showed that this product had a large proportion of tri-ubstituted groups, as did also a commercial methylcellulose prepared from ne conventional alkali cellulose. The distribution of substituent groups in he three methylcelluloses are given in Table 7.

TABLE 7

DISTRIBUTION OF SUBSTITUENT GROUPS IN METHYLCELLULOSE[36]

No. of methyl groups per glucose unit	Methylcellulose from		
	Sodium cupricellulose	Sodium cuprimethylcellulose	Alkali cellulose
0	25.7	..	14.7
1	61.1	21.0	34.7
2	13.1	52.5	41.2
3	0.0	26.5	9.3
Av. methoxyl	15.0	34.6	24.4

(e) *Water-Soluble Ethylcellulose*

The same general considerations with regard to the influence which the dispersing medium for cellulose and the homogeneity of the reaction have upon the degree of substitution required to obtain water solubility apply to ethylation as well as methylation. The principal difference, however, lies in the fact that water solubility is obtained at lower degrees of substitution (Table 6) with ethylcellulose because the larger size of the ethyl group requires that fewer be present to separate the cellulose chains and make the hydroxyl groups available for hydration.

The more hydrophobic nature of the ethyl group, as shown by the generally well-known lesser solubility of ethyl ethers than methyl ethers,[73] also has a bearing on the production of water-soluble ethylcelluloses since the ethylation can easily go too far and water insolubility can result.

The water-soluble ethylcelluloses exhibit the same behavior of gelation upon heating their aqueous solutions as the water-soluble methylcelluloses of D.S. 1.5 or higher. This is to be expected from the known lower hydrogen-bonding power of oxygen attached to ethyl radicals in other compounds.

(*f*) *Hydroxyalkyl Ethers*

A water-soluble stage of etherification is obtained by reaction of ethylene oxide[84] or ethylene chlorohydrin[85] with cellulose[64, 65] or regenerated cellulose[7] in the presence of bases. To get good solubility, NaOH strengths of about 43% are preferred[65] and a ratio of ethylene oxide to cellulose of 0.75 to 1.20 should be used.[64] Cellulose dissolved in quaternary bases may also be used.[42]

Water-soluble hydroxyethylcellulose has had limited industrial use compared to its lower-substituted alkali-soluble form. However, aqueous solutions containing 5% of the commercial product are quite viscous and do not gel upon heating, even to the boiling point. Thus the hydroxyethyl group acts to separate the cellulose chains without decreasing the number of hydroxyl groups available for hydration.

6. Organo-Soluble Alkyl Ethers of Cellulose

The principal organo-soluble cellulose ether from the commercial standpoint is ethylcellulose. It results from interaction of an alkali cellulose prepared from caustic soda of 50% strength or higher with ethyl chloride at elevated temperatures. Information concerning the properties and uses of ethylcellulose may be found in manufacturers' bulletins.[86, 87] Despite the wealth of data on the variation of properties of ethylcellulose with the degree and uniformity of substitution, there exist few reliable data on the variation of physical properties of organo-soluble cellulose ethers as a class with kind or size of substituent group.

(*a*) *Solubility*

The size, polarity, and uniformity of distribution of the substituent groups govern the degree of substitution at which smooth solubility in organic solvents is attained.[74] In the alkyl celluloses, the D.S. at which solubility in alcohol or mixtures of alcohol with aromatic hydrocarbons occurs decreases with the size of the substituent groups as follows: methyl 2.6–2.7; ethyl 2.0–2.2; propyl 1.5–1.7.[44]

The alkyl ethers of cellulose become increasingly soluble in organic

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[84] E. Hubert, German Patent 363,192 (Nov. 4, 1922); E. Hubert and O. Leuchs, German Patent 368,413 (Feb. 5, 1923).

[85] H. Dreyfus, U. S. Patent 1,502,379 (July 22, 1924).

[86] *Ethocel.* Dow Chemical Co., Midland, Mich., 1940.

[87] *Ethyl Cellulose.* Hercules Powder Co., Wilmington, Del., 1941.

solvents with increase in degree of substitution and reach a maximum at a substitution of less than 3. For example, ethylcellulose shows maximum solubility in mixtures of alcohols and hydrocarbons at a D.S. of 2.4 to 2.5, after which solubility in alcohols decreases. This observation can be correlated with increased area of contact between adjoining chains, leading to a large degree of cohesion between them and, hence, greater difficulty of dissolution, as substitution becomes more uniform through completion.[88]

(*b*) *Softening Point*

The degree of substitution at which maximum solubility is obtained is also that of lowest softening temperature of the ether. This is shown in Figure 48 for ethylcellulose and benzylcellulose.

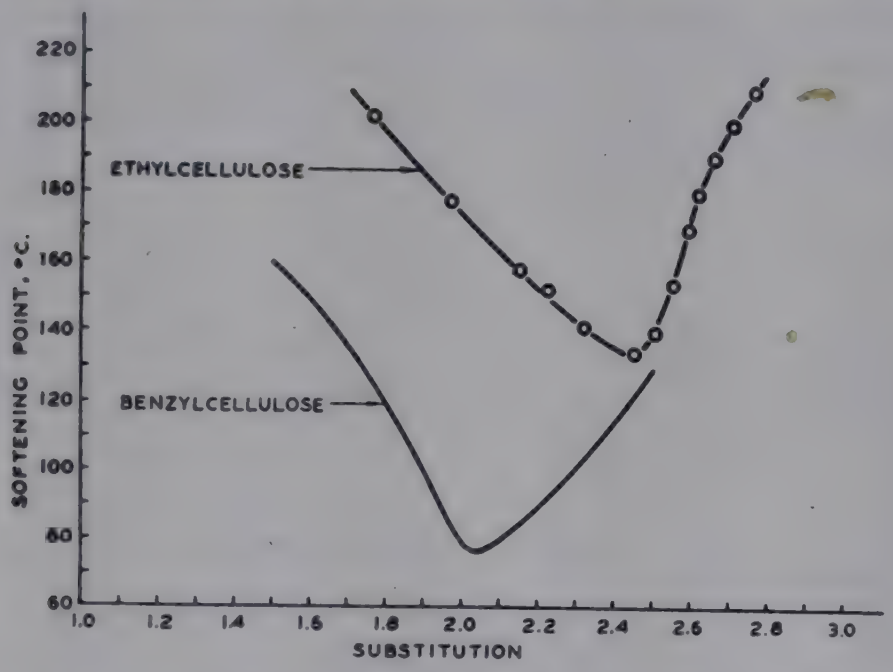

FIG. 48.—EFFECT OF DEGREE OF SUBSTITUTION ON THE SOFTENING POINT OF CELLULOSE ETHERS (LORAND[74]).

The effect of kind and degree of substitution on the softening points of a series of alkyl ethers prepared under identical, mild conditions, to prevent degradation of the cellulose chains and to insure the maximum uniformity of distribution of the etherifying group along the cellulose chains, is presented in Table 8.

Table 8 indicates that increase in size of substituent group (the factors of uniformity, degree of substitution to reach organo-solubility, and specific viscosity being the same for each derivative) brings about decrease in softening point, just as in the case of the cellulose esters.

[88] E. Ott, *Ind. Eng. Chem.*, **32**, 1641 (1940).

TABLE 8

SOFTENING POINTS OF A SERIES OF ALKYL ETHERS OF SIMILAR SOLUBILITY CHARACTERISTICS PREPARED IN LIQUID AMMONIA (DOW CHEMICAL COMPANY[44])

Cellulose ether	D.S.	Softening point, °C.	Solubility in			
			Methanol	Benzene	Ligroin	67 : 33 Benzene : methanol
Methyl	2.8	193	Insoluble	Swells	Insoluble	Soluble
Ethyl	2.3	166	Insoluble	Swells	Insoluble	Soluble
Propyl	1.5	168	Insoluble	Swells	Insoluble	Soluble
Butyl	1.8	143	Insoluble	Swells	Insoluble	Soluble
Amyl	1.8	120	Insoluble	Swells	Swells	Soluble

In the case of an individual cellulose ether, the higher the average chain length, as measured by specific viscosities, the higher will be the softening point of the product, other factors being kept as constant as possible. This is indicated by the data in Table 9.

TABLE 9

EFFECT OF SPECIFIC VISCOSITY ON SOFTENING POINT (LORAND[74])

Cellulose ether	D.S.	Specific viscosity	Softening point, °C.
Ethyl	2.16	0.132	99
Ethyl	2.14	1.267	162
Ethyl	2.52	0.229	112
Ethyl	2.50	2.847	144
Benzyl	2.20	0.362	68
Benzyl	2.20	1.183	104

If the substituent group itself is highly polar, with consequent stronger force of association between chains, the softening point of the ether will be increased. Thus, Lorand[74] found that an ethyl(hydroxyethyl)cellulose had a softening point of 152°C. as compared with 142°C. for a similar ethylcellulose.

(*c*) *Tensile Strength*

The strength properties of cellulose ethers completely parallel the softening properties. Thus, methylcellulose, both by virtue of the polarity of the methyl group itself and its small size, yields the strongest and hardest films of any of the alkyl celluloses (Fig. 49). The curves also show that the

yield points of the films decrease as the length of the substituent group increases, indicating increasing softness with the higher alkyl ethers.

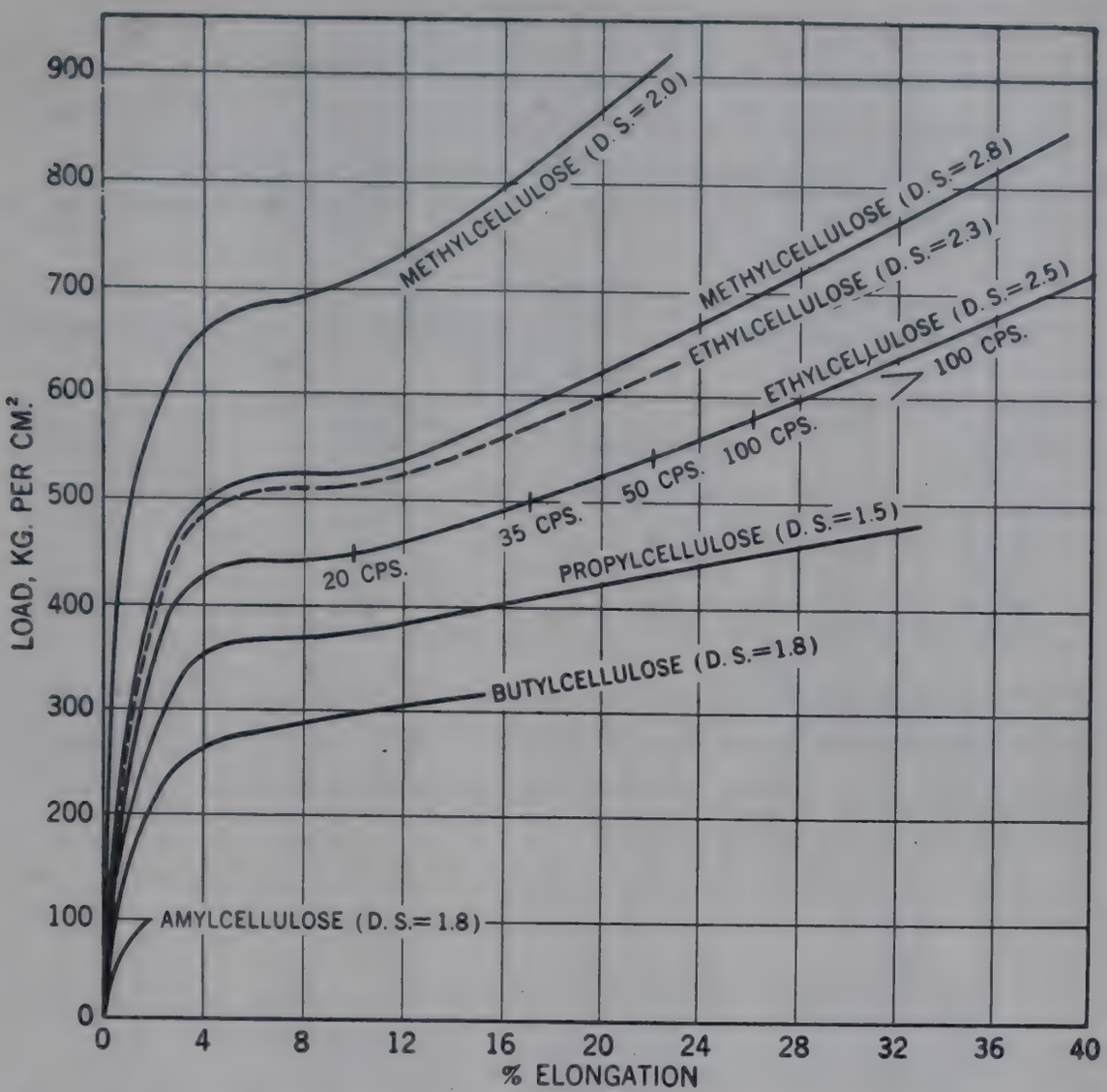

FIG. 49.—LOAD-ELONGATION CURVES OF ORGANO-SOLUBLE ALKYL ETHERS OF CELLULOSE (DOW CHEMICAL CO.[44]).

(*d*) *Correlation of Physical Properties*

The above-stated differences in solubility, softening point, and tensile strength of cellulose ethers are a natural outcome of progressive destruction of hydrogen bridges through increasing separation of cellulose chains due to substitution. Uniform substitution of low degree, logically, may cause the same over-all amount of separation as a higher degree of substitution which is less uniform. Similarly, a smaller amount of substitution with large groups may cause the same amount of prying apart of macromolecules as a larger amount of small substituent groups. The greater the average over-all distance between cellulose chains, the lower will be the tensile

strength and softening point of the cellulose derivative and the greater will be its degree of solubility.

(e) *Water Sorption*

As might be expected, the amount of water absorbed by a given cellulose alkyl ether under standard conditions is a function of both the number of free hydroxyl groups and the molecular size of the substituent group. The effect of the latter is shown in Table 10, in which the sorption of water

TABLE 10

EFFECT OF SUBSTITUENT GROUP ON MOISTURE SORPTION OF CELLULOSE ETHERS (LORAND[74])

Cellulose ether	Substitution	Softening point, °C.	% Moisture absorption, 72% R.H. at 19°C.
Ethyl	2.15	158	3.001
Butyl	2.28	65	1.673
Amyl	1.91	45	0.975

vapor by three ethers of nearly the same degree of substitution are compared at 72% relative humidity at 19°C.[74] For a given ether, the relation of moisture sorption to degree of substitution is indicated by the series of curves compiled in Figure 50.

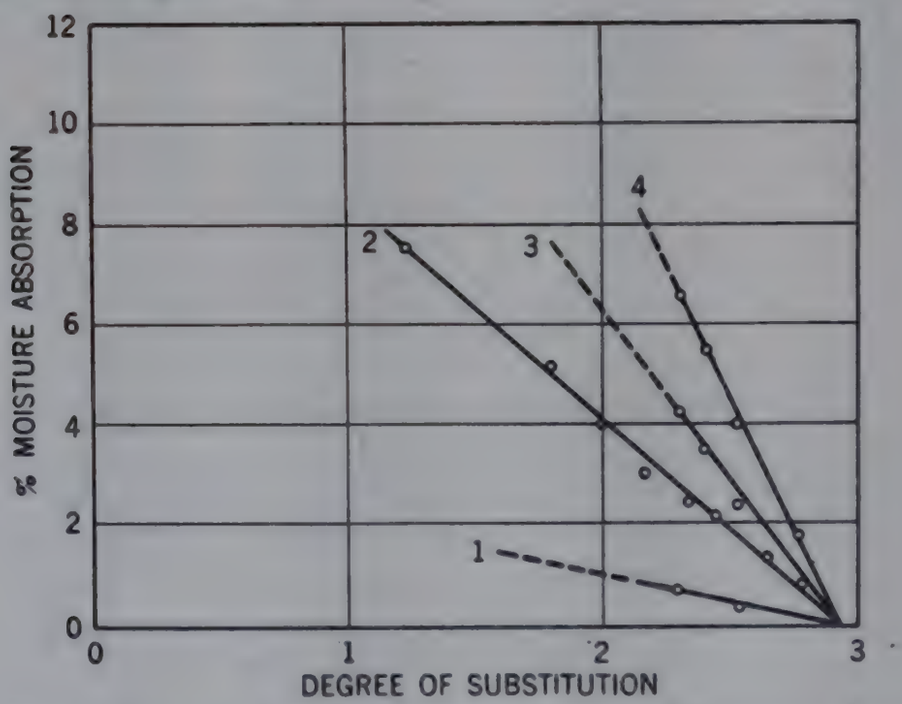

FIG. 50.—EFFECT OF DEGREE OF SUBSTITUTION ON THE MOISTURE ABSORPTION OF ETHYLCELLULOSE (DOW CHEMICAL CO.[44]).

Curves: 1, 50% relative humidity at 21°C.; 2, 70% relative humidity at 19°C.; 3, immersion in water at 50°C.; 4, immersion in water at 21°C.

The moisture transmission through thin films of a series of alkyl ethers is shown in Figure 51. The transmission data were determined on films of 1 mil thickness with atmospheres of 100% and 0% relative humidities being maintained on opposite sides of the film.

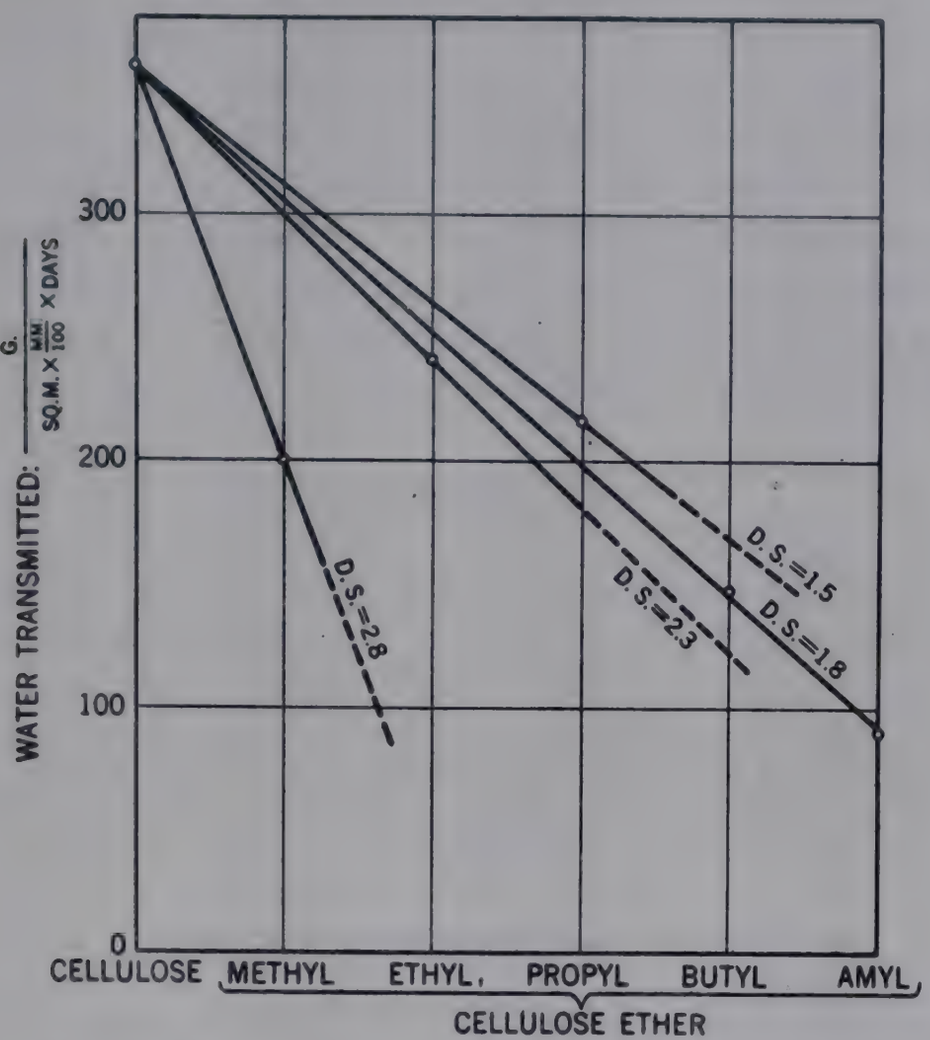

FIG. 51.—EFFECT OF DEGREE OF SUBSTITUTION OF CELLULOSE ETHERS ON THE WATER TRANSMISSION THROUGH THEIR FILMS (DOW CHEMICAL CO.[44]).

(f) *Commercial Utility of Ethylcellulose*

The highly-substituted organo-soluble ethers find application in the plastics, film, and lacquer industries. For these uses, tensile strength, hardness, and softening point must be relatively high, and wide solubility characteristics and low moisture absorption are also important. The ether which possesses the best combination of these properties is ethylcellulose of D.S. 2.2–2.6, and this is the only organo-soluble cellulose ether made commercially in the United States. In common with all other cellulose ethers, ethylcellulose is extremely stable to saponification treatment.

Ethylcellulose is a base material which is increasing rapidly in industrial importance in the manufacture of coatings, films, and plastics. As a coating material, it is unusual in its compatibility with resins and plasticizers and its solubility in mixtures of alcohols with hydrocarbons. It can also be used in the form of hot-melt coatings in which ethylcellulose acts as a toughening agent for blends of waxes and resins. Ethylcellulose film and sheeting is tough and highly flexible, especially at subzero temperatures. In ethylcellulose plastics, this retention of flexibility is preserved through proper choice of plasticizers. Since ethylcellulose is thermoplastic at temperatures lower than cellulose esters, it requires less plasticizer to become moldable. Ethylcellulose plastics are especially suited to extrusion or injection molding and are particularly useful for wire insulation and molded shapes which must remain tough and flexible at low temperatures.

7. Other Ethers of Cellulose

Among the other cellulose ethers, the benzyl and the triphenylmethyl ("trityl") ethers deserve brief mention. The former has had some small industrial importance, especially in Europe, while the latter is of distinct laboratory interest. In addition to these ethers, one other, butylcellulose, has been introduced in France on a commercial scale, but there is little information concerning its special properties.

(*a*) *Benzylcellulose*

Benzylcellulose is prepared, like the other ethers, by the action of benzyl chloride on alkali cellulose in the presence of a large excess of caustic. The product is alkali-insoluble at all stages of the etherification, so the reaction is entirely heterogeneous in nature.[22, 89]

Benzylcellulose was developed to a commercial stage in Europe earlier than ethylcellulose. Economic conditions favored its preparation because of the high relative cost of ethyl chloride to benzyl chloride in continental Europe where cheap alcohol or ethylene was not available for manufacture of the etherifying agent. It has excellent water resistance and good electrical properties, but its low softening point and extreme sensitivity to light and heat limit its usefulness in the exacting applications open to cellulose derivatives today.

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[89] K. Brandt, Dissertation, Berlin, 1933.

(*b*) *Tritylcellulose*

When triphenylchloromethane reacts with alkali cellulose, an ether is formed which is found to have a D.S. of approximately 1.0 and which is readily split into its components by aqueous hydrochloric acid. Helferich and Koester,[90] who first investigated this compound, came to the conclusion that only the primary hydroxyls etherified, and this premise was adopted and used by others, including Sakurada,[91] as the basis of a means of preparing cellulose esters having the primary hydroxyls free. The method consisted in making the trityl ether, esterifying it completely, and then splitting off the trityl groups with acid. Recently, a question has been raised as to the specificity of the attack on the number 6 position,[92, 93] but it does seem likely that it is steric hindrance caused by the large triphenylmethyl groups which prevents the D.S. from rising to more than 1.0.

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[90] B. Helferich and H. Koester, *Ber.*, **57B,** 587 (1924).

[91] I. Sakurada and T. Kitabatake, *J. Soc. Chem. Ind.* (*Japan*), **37,** B604 (1934).

[92] R. C. Hockett and C. S. Hudson, *J. Am. Chem. Soc.*, **56,** 945 (1934).

[93] F. B. Cramer and C. B. Purves, *J. Am. Chem. Soc.*, **61,** 3458 (1939).

F. XANTHATES

EMIL KLINE

When cellulose is treated with sodium hydroxide solution of mercerizing strength to form so-called alkali or soda cellulose (see Section D of this chapter) and this soda cellulose is then treated with carbon disulfide, interaction occurs with the formation of a sodium salt of the cellulose ester of dithiocarbonic acid, more familiarly known as cellulose xanthate. The formation of this ester of cellulose is broadly represented as follows:

$$R_{cell}\text{—}ONa + CS_2 \longrightarrow R_{cell}\text{—}O\text{—}\underset{\underset{S}{\|}}{C}\text{—}SNa \qquad (1)$$

This reaction, which was discovered in 1892 by Cross, Bevan, and Beadle,[1] is known as the "viscose reaction" from the high viscosity of the solution of the xanthate in dilute sodium hydroxide ("viscose"). It is one of the most interesting reactions of cellulose and, because of low cost, industrially one of the most important. Unlike most of the other cellulose derivatives, however, the xanthate is not of interest for itself but only as a means of solubilizing cellulose, from which solution the cellulose may be regenerated in almost any desired shape or form. The viscose process has thus found use in the production of rayon, staple fiber, cellophane, sausage casings, bottle caps, artificial sponges, sizings, etc., and has become the leading process in the manufacture of these products. The industrial importance of the process will be appreciated when it is considered that in 1940 over 2,000,000,000 pounds of finished products, valued, by U. S. standards, at approximately $750,000,000, were produced from viscose. These products required the preparation of about 12,000,000 tons of viscose.

Since the changes in cellulose upon reaction with carbon disulfide, and the regeneration of the cellulose from the viscose solution are of interest chiefly as carried out industrially in the "viscose process," the xanthates will be discussed mainly from this viewpoint.

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[1] C. F. Cross, E. J. Bevan, and C. Beadle, *Ber.*, **26**, 1090 (1893); C. F. Cross and E. J. Bevan, *Ber.*, **34**, 1513 (1901); C. F. Cross, E. J. Bevan, and C. Beadle, U. S. Patent 520,770 (June 5, 1894); Brit. Patent 8700 (Feb. 6, 1893).

1. The Preparation of Viscose

(a) *Small-Scale Laboratory Method*

The conventional procedure for the preparation of viscose involves a series of steps. Alkali or soda cellulose is first produced by steeping cellulose in caustic soda solution, pressing to remove the excess liquor, shredding, and aging to the desired viscosity. The alkali cellulose is then xanthated by reacting with carbon disulfide, and the xanthate is dissolved in dilute sodium hydroxide solution. The viscose thus produced is filtered, subjected to a vacuum treatment, and ripened to the desired point, after which it is ready for use. These operations may be carried out on a small scale as follows:

Place 100 g. (about 7 sheets, 6 in. by 6 in.) of air-dry, rayon-grade, "low-alpha" sulfite cellulose sheets (see Table 1) edgewise in a rectangular nickel tank or glass battery jar (7 in. wide by 7 in. high by 2.5 in. long) in a water bath, at 21 °C. Fill the tank slowly to about 1 in. above the pulp with 18.0% NaOH solution (see Table 2), previously adjusted to 21 °C. Allow the pulp to remain in the caustic solution for 1 hr., maintaining the temperature constant at 21 °C. ± 0.5 °C.

Siphon or pour off the caustic. Stack the steeped sheets carefully on a perforated nickel plate and cover with another similar plate. Place the plates and the alkali cellulose in a laboratory hydraulic or hand "letter" press and press to a weight of 300 g. Shred the pressed sheets in a small Werner-Pfleiderer shredder for 2 hrs., maintaining the temperature at 21 °C. ± 0.5 °C., and then place the shredded alkali cellulose in a two-quart glass fruit jar. Seal and place the jar on mechanical rollers in a water bath at 21 °C. Allow the soda cellulose crumbs to age for 65 hrs. under these conditions (constant rotation at 21 °C. ± 0.5 °C.).

After aging, add 32 g. of CS_2, reseal, and replace the jar on the mechanical rollers in the water bath. Allow the mass to rotate for 3 hrs. at 21 °C. ± 0.5 °C. When the reaction with CS_2 has been completed, remove the jar from the rolls, evacuate it to remove any excess CS_2, then add 169 g. of 18% sodium hydroxide solution and 764 g. of water. Stir with a mechanical agitator (nickel or stainless steel) for 2 hrs., until solution is complete, still maintaining the temperature constant at 21 °C. ± 0.5 °C. This will give about 1265 g. of viscose containing 7% cellulose and 6% NaOH, with a viscosity of 40 to 50 poises and a total sulfur content of about 2.0%. After adequate filtration and ripening (see p. 818), the viscose will be comparable to a commercial solution and useful for the preparation of filaments, films, etc.

As will be clear from the discussion which is to follow, exact specifications covering viscose composition, alkali cellulose aging time, and viscosity cannot be stated without identifying in detail the type of cellulose, caustic, etc. If the desired viscose composition and viscosity are not obtained, duplicate runs should be made in which the alkali cellulose is analyzed for per cent of cellulose and per cent of NaOH, and the alkali cellulose aging time varied. From the analysis of the alkali cellulose, the correct amounts

of NaOH and water to be added to the xanthate can be calculated. By plotting the logarithm of the alkali cellulose aging time against the logarithm of the viscose viscosity for two, three, or more runs, straight-line relationships are obtained from which the exact time for any given viscosity can be determined.

If cellulose is not available in the form of sheets, viscose can be prepared from bulk pulp, or from a good grade of absorbent cotton, by carrying out the steeping operation in a beaker or any suitable vessel equipped with an agitator. The ratio of 18% caustic solution to cellulose should be about 25 to 1. After the treatment with caustic, the excess liquor may be removed from the bulk pulp contained in a cloth bag by centrifuging or pressing, and then proceeding as described above.

(*b*) *Large-Scale Manufacture*[2]

Preparation of Alkali Cellulose.

Raw Materials. The principal raw materials entering into the manufacture of viscose are cellulose, sodium hydroxide, and carbon disulfide. Of these, cellulose is the most important because it also constitutes the end-product of the process. At the present time the only practical sources of cellulose are cotton and wood. Other possible cellulosic materials, such as bagasse and cornstalks, are satisfactory, but to date they have been too expensive to refine to the point required by the process. When cotton is the source of cellulose, it is obtained mainly from second-cut linters and hull fiber (see Chapter VI, B). Wood cellulose (from which by far the greatest part of the world's output of viscose products is produced) is derived chiefly from spruce and Western hemlock, although very satisfactory pulps are also being produced from Southern pine and from certain of the hardwoods. Actually, the kind of wood is secondary in importance to the methods used to isolate and purify the cellulose (see Chapter VI, A). For this purpose the sulfite process is employed almost exclusively.

The factors which generally determine the type of cellulose to be used in the manufacture of viscose are the type of product to be produced (rayon, cellophane, staple, etc.), the quality of product, price, and alkali cellulose aging facilities. Where strength, durability, and toughness are the prime considerations (such as in the manufacture of high-tenacity

[2] V. Hottenroth, *Artificial Silk.* Pitman, London, 1928; E. Wheeler, *The Manufacture of Artificial Silk.* Van Nostrand, New York, 1931; M. H. Avram, *The Rayon Industry.* Van Nostrand, New York, 1929; O. Faust, *Kolloidchem. Tech.*, No. 2, 124 (1931).

rayon, sausage casings, bottle caps, etc.), pulps high in alpha-cellulose content, including cotton linters, are necessary, or, at least, are desirable.[3] Where these requirements are not quite so important, or where price is a deciding factor, the lower-alpha or poorer-color pulps are used. While most pulps are produced in what might be described as a "medium" range of viscosity, special "low-viscosity" pulps have come into use in recent years requiring only one-half to one-third of the aging time of the

TABLE 1

REPRESENTATIVE ANALYSES OF VISCOSE PULPS[a]

Group	Low-alpha wood pulps	High-alpha wood pulps	Cotton linters pulps	Low-viscosity wood pulps
% Alpha-cellulose	88.0 –92.0	94.0 –96.0	98.0 –99.0	87.0 –92.0
% Beta-cellulose	3.0 – 4.0	2.0 – 3.0	1.0 – 1.5	5.0 – 8.0
% Gamma-cellulose	4.0 – 9.0	1.0 – 4.0	0.0 – 1.0	3.0 – 5.0
% Ash	0.03 – 0.10	0.04 – 0.08	0.07– 0.12	0.07 – 0.12
% Silica	0.003– 0.005	0.003– 0.005	0.05	0.003– 0.01
% Calcium	0.01 – 0.05	0.02 – 0.05	0.02	0.005– 0.05
Iron, p.p.m.	4 – 10	3 – 6	10 – 15	3 – 12
% 10% KOH-soluble	14.0 –18.0	4.0 – 6.0	2.0 – 4.0	8.0 –22.0
% Ether extract	0.10 – 0.30	0.07 – 0.12	0.10– 0.20	0.10 – 0.20
Cuprammonium viscosity, cps. (A. C. S. method)	400 – 800	400 – 800	250 – 500	100 – 150

In addition to the above analytical characteristics, the amounts of other metallic impurities such as copper, manganese, etc., are also of importance and should be as low as possible. Since viscose viscosity does not always parallel cuprammonium viscosity, the viscosity figures do not necessarily reflect directly the alkali cellulose aging times required for the various pulps.

[a] Unpublished data compiled from analyses by du Pont Co. and by pulp vendors.

medium-viscosity pulps. The various types of pulps on the market may be divided into four groups according to alpha-cellulose content and cuprammonium viscosity; representative analyses are given in Table 1.

It should be understood that a chemical analysis alone of a pulp is not sufficient to establish its value as a source of cellulose for viscose. As a matter of fact, exact specifications covering the cellulosic raw material cannot be set up, since complete information is still lacking correlating all of the various characteristics of a pulp with the process and product. Above all, the pulp must be uniform at all times, in all respects, including

[3] O. P. Golova, *Kunstseide*, **17**, 302 (1935).

chemical analysis, viscosity, color, sheet structure, etc., and the only way to reach a final conclusion regarding the utility of a given type of cellulose is actually to convert it into viscose and into the particular end-product (filaments, films, etc.) desired.[4]

The principal considerations in connection with the caustic soda used in the viscose process are the impurities which may be present, mostly metallic salts, which affect the viscosity, color, and solubility of the xanthate, and certain characteristics of the final product. It is important that all metallic impurities be uniform and as low as possible in concentration. These impurities vary slightly depending upon the type of caustic

TABLE 2

REPRESENTATIVE ANALYSIS OF A 50% CAUSTIC LIQUOR[a]

Material	%	Material	P. p. m.
		Fe	3–6
NaOH	50.0 – 50.5	Ca	1–15
Na_2SO_4	0.001 – 0.08	Al	10–20
Na_2CO_3	0.05 – 0.20	Mg	5–15
NaCl	0.05 – 0.20	Mn	0.3–0.5
SiO_2	0.005 – 0.02	Cu	0.3–0.6
		Ni	0.0–0.5

[a] Unpublished data compiled from analyses by du Pont Co. and by caustic vendors.

(caustic liquor versus solid caustic; and ammonia-soda process versus electrolytic process), although most producers have now so refined their operations and reduced all impurities that there is practically no significant variation in chemical analysis from one producer's material to another. Caustic is usually supplied in the form of 50% liquor, in specially lined tank cars. The use of 73% liquor also has been introduced recently, and solid caustic, which was employed almost universally some years ago, still finds some use, particularly where caustic must be transported over long distances. The range of impurities usually found in 50% caustic liquor is shown in Table 2.

The carbon disulfide used for viscose is an almost chemically pure product produced by the direct interaction of carbon and sulfur under definite conditions. There is usually no need for concern over specifications and impurities.

[4] C. H. Goldsmith, *Rayon and Melliand Textile Monthly*, **16**, 513 (1935); K. Fabel, *Kunstseide*, **17**, 42 (1935).

Steeping. As indicated above, the first step in the viscose process is the treatment of the cellulose raw material with sodium hydroxide solution of mercerizing strength. This treatment, known as the steeping operation, has two specific and distinct objectives: (1) the uniform and complete formation of alkali or soda cellulose I (swelling and absorption of NaOH), and (2) the removal of hemicellulose and other impurities from the cellulose.

In conventional industrial operation, the cellulosic raw material (pulp), in the form of sheets, is placed edgewise in a steeping press, that is, a rectangular tank, with a ram at one end actuated by a screw or hydraulic pressure (see Fig. 52). The size of the press charge varies considerably. In the United States, batches of 100 to 200 lbs. are normal, the sheets averaging 17 in. by 19 in. and 0.030 in. thick. In Europe, charges as large as 2000 lbs.[5] are said to be in use, with sheet sizes up to 30 in. by 40 in. The press is filled slowly with caustic solution containing 18% NaOH and 0.5 to 1.5% hemicellulose and the reaction allowed to proceed for 30 to 60 minutes at a definite temperature, the normal range being 15–30 °C. (The reaction being exothermic, a rise in temperature of 2–3 °C. usually occurs.)

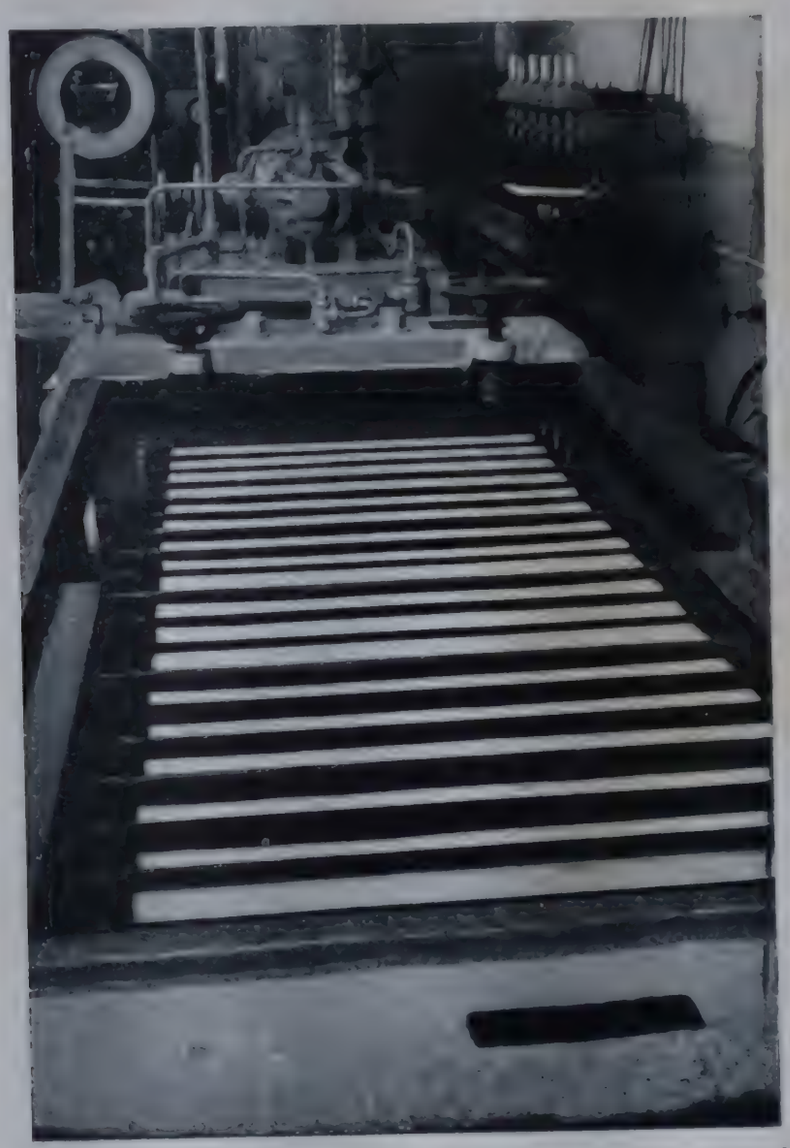
Of the factors that control the steeping operation, time, temperature, and concentration of NaOH are all-important. For the formation of soda cellulose I the concentration of NaOH must lie in the region in which soda cellulose I is stable, that is, 14 to 20% NaOH. When the operation is carried out in a conventional steeping press, 18% NaOH usually gives the best results. Deviations from this concentration of the order of ±1–2% may not be particularly harmful if suitable adjustments are made, but neither are they advantageous except in specific instances. Swelling of the pulp varies with NaOH concentration; the lower the concentration, the higher the swelling. The NaOH concentration also affects the composition and the rate of aging of the soda cellulose; the higher the NaOH, the faster the aging.

Temperature is important in steeping mainly because of its effect on swelling, which decreases with increasing temperature. Higher temperatures therefore result in lower hemicellulose losses, higher yield, stronger steeped sheets, less slumping in the press, easier pressing, etc. Lower temperatures, on the other hand, increase the absorption of caustic and are important where increased swelling is desirable. Steeping temperature also affects viscose viscosity, viscose ripening, and alkali cellulose composition.

Since mercerization is a relatively rapid reaction, time of steeping is determined largely by the time necessary to solubilize and remove the

[5] H. Jentgen, *Kunstseide*, **18**, 408 (1936)

hemicellulose and other impurities from the pulp. As much as 15 minutes is required to remove the main portion of hemicelluloses from some pulps in a conventional steeping press, hence this may be considered about the



Courtesy of Rayonier Incorporated

FIG. 52.—STEEPING OPERATION.

Sheets (30 in. by 20 in.) of sulfite wood cellulose being converted to alkali cellulose by treatment with 18% NaOH solution in a conventional commercial steeping press.

minimum permissible time. Additional time is not objectionable, and 30 to 60 minutes (in some instances 2 hrs.) are usually employed.

Some of the other variables[6] which affect the conventional steeping

[6] *Steeping Procedure.* Rayonier Incorporated, San Francisco, April, 1941.

operation are concentration of hemicellulose, pulp sheet density (the number of sheets per inch in the press), rate of filling of the steeping press, pulp sheet formation and structure, and use of wetting agents. The amount of hemicellulose present influences the uniformity of mercerization, the rate of alkali cellulose aging and xanthation, the solubility of the xanthate, the rate of viscose ripening, and the characteristics of the final product. It is desirable that the hemicellulose content of the steeping solution be kept low. It is not feasible economically, however, to discard the caustic used in the operation; hence, it is almost universal practice to return it to the process and to remove the hemicellulose from a portion of the solution by dialysis, thus maintaining a constant, fairly low concentration of hemicellulose in the steeping liquor. Although it has been proposed to add various other materials to the steeping solution, including wetting agents (which improve caustic penetration and shredding, thus giving more uniform xanthation and improved solution), sodium sulfide and oxidizing agents (for reducing viscosity), alcohols, proteins, starch, etc., few, if any, of these have found practical use.

Pressing. Since caustic soda reacts with carbon disulfide to form useless by-products (see below), it is desirable to remove as much excess caustic as possible from the alkali cellulose before this reaction. For this reason, after steeping, the solution is drained from the tank and the steeped pulp is pressed to about three times the weight of the original air-dry pulp. As indicated, the waste solution, containing the hemicellulose removed from the pulp, is dialyzed and used over again.

The ease of pressing is inversely proportional to the degree of swelling and, hence, is determined by type of pulp, temperature, and concentration of NaOH. The pressing factor or press weight ratio (ratio of weight of pressed alkali cellulose to original air-dry pulp) controls the composition of the alkali cellulose as well as of the waste caustic solution. Using an ordinary rayon grade pulp (91% alpha-cellulose) and 18% NaOH solution, a press weight ratio of 3.0 to 1.0 gives an alkali cellulose containing approximately 29.8% cellulose, 15.2% NaOH, 55% H_2O. Changing the press weight ratio changes the cellulose content, the NaOH content remaining nearly constant. At a press weight ratio of 2.5 to 1.0, for example, the analysis is about 35% cellulose, 15% NaOH, 50% H_2O.

The press weight ratio also influences shredding, the rate, efficiency and uniformity of xanthation, the rate of degradation of the cellulose during alkali cellulose aging, and the properties of the final product. The lower the ratio, the poorer is the shredding and the slower is the alkali cellulose aging and the rate of carbon disulfide absorption. However, xanthation is

more efficient at the lower ratios, and solubility is improved, provided shredding is satisfactory. In commercial operation, the pressing factors employed are in an intermediate range (2.7 to 1–3.2 to 1), which represents a compromise between poor shredding and low reaction rate on the one hand and gelatinization of the fibers on the other.

Shredding. After removal of the excess caustic by pressing, the alkali cellulose is mechanically disintegrated or shredded for 1 to 3 hrs. at 25 to 35°C. to form a mass of fibers resembling bread crumbs. This serves to increase the surface of the alkali cellulose and insure rapid and uniform aging and xanthation. To achieve further uniformity and low cost, it is customary to combine two or more steeping press charges into a single shredder charge. The operation is conventionally carried out in equipment resembling a dough mixer, that is, a Werner-Pfleiderer shredder, which tears the sheets between rapidly rotating blades and a stationary saddle.

Optimum shredding is indicated by a maximum of fibrillation without agglomeration or knot formation. Although various tests have been devised for evaluating shredding, such as determination of particle size and density, none are really significant. In addition to the factors already mentioned, time and temperature must be carefully controlled, not only to secure optimum shredding, but also to control the degradation of the cellulose which always occurs during this stage.

Aging of Alkali Cellulose. Following shredding, the alkali cellulose crumbs are placed in covered cylindrical or rectangular steel containers, in a constant-temperature room, and allowed to "age" for 1 to 3 days at 25 to 30°C. During this step (see Section D of this chapter) absorption of oxygen occurs and the viscosity of the cellulose is reduced. This reduction in viscosity is required, since the solution viscosities which would otherwise be obtained from present-day, unaged, commercial celluloses would be considerably higher than desired. The rate and extent of the viscosity reduction during aging are controlled by temperature and time; the higher the temperature the faster the aging, and the longer the time the lower the viscosity. Other factors influencing aging include type of cellulose, presence of metallic impurities such as iron and manganese, xanthation conditions, and viscose composition. The former use of small containers has given way largely to containers that hold an entire shredder charge (600 lbs. or more of alkali cellulose). In some operations the aging step has been further simplified and/or shortened by the use of low-viscosity pulps, aging before shredding, high-temperature shredding, etc.

Xanthation of Alkali Cellulose. This is the most significant step in the making of viscose, since here the actual conversion of the cellulose to a

soluble derivative takes place. For this purpose, the aged alkali cellulose is placed in a hexagonal or cylindrical rotating drum, and carbon disulfide is slowly admitted as a gas or liquid through a perforated pipe within the drum. The reaction is permitted to continue for 1 to 3 hrs., in the temperature range 20–35°C., either at atmospheric pressure or under vacuum. The quantity of carbon disulfide added is usually between 30 and 40%, based on the cellulose in the alkali cellulose. As the reaction proceeds, the white alkali cellulose gradually becomes yellow and finally assumes an

Courtesy of du Pont Co.

FIG. 53.—CELLULOSE XANTHATE.

Unloading and dumping a drum in which alkali cellulose has been formed into cellulose xanthate through reaction with carbon disulfide at a cellophane cellulose film plant.

orange or "carrot" color. The end-product usually retains some of its original crumbly, mealy character although it is somewhat sticky; its actua color and physical characteristics are determined in part by the al ali cellulose composition, the carbon disulfide concentration, and the temperature and time of reaction (see Fig. 53).

Several of the factors influencing the xanthation reaction have been mentioned. It may be added that (1) the nature of the cellulose affects both the rate of xanthation and the amount of carbon disulfide required to produce good solubility; (2) the uniformity of carbon disulfide distribution is

important for good solubility; (3) the rate of xanthation is proportional to the vapor pressure of the carbon disulfide and the temperature; (4) the maximum degree of xanthate substitution decreases with increase in temperature, but solubility increases with increase in temperature in the range 15–35°C.; (5) the time of reaction should be sufficient for complete absorption of carbon disulfide, but solubility does not improve on further standing; (6) the solution viscosity of the cellulose is markedly reduced by oxidation during xanthation, hence temperature and presence of oxygen are important factors; (7) the stability of the xanthate decreases with increase in temperature, increase in press weight ratio, increase in degree of xanthation, and increase in hemicellulose content; and (8) xanthation conditions, particularly temperature, carbon disulfide concentration, and degree of xanthation, influence regeneration and the characteristics of the final product.[7]

At the end of the xanthation reaction the excess carbon disulfide is removed by evacuation, and the mass is dissolved in dilute sodium hydroxide solution to form the final solution—viscose. To achieve greater uniformity, two batches of xanthate (four steeping press charges) are often combined at this point to form a single charge. The amounts of NaOH and water employed in preparing the final solution depend upon the alkali cellulose analysis and the viscose composition (% cellulose and % NaOH) desired. The latter varies with different producers and with the type of end-product, although the concentrations are usually in the range of 6.0 to 10.0% cellulose and 4.0 to 8.0% NaOH. Assuming an alkali cellulose composition of 29.8% cellulose and 15.2% NaOH, press weight ratio of 3:1, 35% carbon disulfide, and the combination of four steeping press charges of 150 lbs. of pulp each, the production of a viscose solution containing 7% cellulose and 6% NaOH would require 5490 lbs. of water and 186 lbs. of 100% NaOH, giving a total viscose weight of about 7650 lbs.

Dissolving of the xanthate is referred to as the "mixing" step from the fact that it is carried out by simply mixing the xanthate and caustic soda solution in a large cylindrical tank (Vissolver) equipped with an agitator. The mixing operation normally requires from 2 to 6 hrs., the temperature being controlled in the range 15–20°C.

Ripening of Viscose Solutions. As initially prepared, viscose is relatively difficult to coagulate and, hence, is not suitable for most industrial opera-

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[7] P. C. Scherer and coworkers, *Rayon Textile Monthly*, **19**, 478, 541 (1938); **20**, 24, 81, 498, 577 (1939); **21**, 529, 611 (1940); W. Schramek and E. Zehmisch, *Kolloid-Beihefte*, **48**, 93 (1938).

tions. To make it fit for spinning, casting, etc., it is transferred (usually after further blending) to large tanks in another constant-temperature room where it is stored under controlled conditions of time and temperature to permit "ripening." During this period various changes occur, the most important being spontaneous decomposition of the xanthate and an increase in ease of coagulation of the solution. However, since these changes continue until coagulation and regeneration of the cellulose are complete, the viscose cannot be stored indefinitely but must be used within a few days after preparation.

For any given viscose, the rate at which ripening occurs is governed by temperature, the higher the temperature the faster the ripening. (Ripening is an exothermic reaction and the temperature coefficient is high.) The extent of the ripening (and hence time) is determined (empirically) by the regenerating conditions to be used and by the use to which the viscose is to be put, that is, whether it is to be spun into threads, cast into films, etc. Coagulating methods have been developed in recent years which permit the use of relatively "unripe" or "green" viscose, but in most operations ripening requires 1 to 3 days, the normal temperature range being 15–20°C.

During this period, various analyses also are carried out, the viscose is filtered (usually in two or more stages, using plate and frame filter presses dressed with various combinations and types of cotton fabric and cotton batting), and finally evacuated, to remove air. When the ripening has reached the point required for conversion to the particular end-product desired, the viscose is ready for use.

Continuous and "Quick" Processes. Other methods for preparing viscose, and particularly alkali cellulose, have recently come into use, or have been suggested, which are cheaper or which overcome some of the objections to the multiple-stage operation just described. These involve mostly continuous methods of operation or a reduction in the number of stages. In certain operations, also, pulp is treated in bulk form in tanks equipped with suitable agitators, and the excess caustic removed by centrifuging or by suitably designed presses or press rolls. This type of procedure, starting with either sheets or bulk pulp, may be carried out continuously. Another continuous-type procedure involves the passing of pulp in sheets or in roll form on a conveyor through a caustic solution, followed in some cases by continuous shredding, aging, xanthation, and solution. If the viscose plant is erected adjacent to the pulp plant, the pulp may be employed without drying. Other variations involve countercurrent steeping, spraying the pulp with caustic in a shredder, and treat-

ment with carbon disulfide in the presence of an inert organic solvent or at extremely low temperatures.[5, 8]

2. The Mechanism of Cellulose Xanthate and Viscose Formation

On the basis of the analogy between cellulose and ordinary alcohols, the reaction between soda cellulose and carbon disulfide was first represented in a manner similar to the reaction between carbon disulfide and alcohols in the presence of alkali. It has been known for a long time that when ethyl alcohol is treated with CS_2 in the presence of KOH, potassium ethyl xanthate is formed, the reaction being as follows:

$$C_2H_5OH + KOH + CS_2 \longrightarrow C_2H_5{-}O{-}\overset{\overset{S}{\|}}{C}{-}SK + H_2O \qquad (2)$$

Similar compounds are formed with other alcohols, including polyhydric alcohols. If cellulose is substituted for the ethyl alcohol in equation (2), the analogous reaction product is sodium cellulose xanthate[9] as shown in equation (1).

This equation, however, may be considered only as a simple, general expression of the viscose reaction. The actual reaction is of a colloidal nature and is far more complicated. It has been the subject of numerous investigations,[1, 7, 10] which have now answered many of the questions concerning the mechanics and chemistry involved, although further study of the reaction is still desirable.

Unlike many of the other cellulose derivatives such as the trinitrate

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[8] H. Jentgen, *Kunstseide u. Zellwolle*, **20**, 449 (1938); R. Monterray, *Rusta-Rayonne*, **13**, 517 (1938); *Rayon Textile Monthly*, **18**, 227 (1937); H. Schmidt, *Chem. Fabrik.*, **4**, 73, 85, 97 (1931); F. Steimmig, U. S. Patent 2,005,811 (June 25, 1935); German Patent 604,015 (Oct. 17, 1934); French Patent 751,617 (Feb. 27, 1933); H. von Kohorn zu Kornegg, U. S. Patent 2,218,836 (Oct. 22, 1940); G. A. Richter, U. S. Patent 1,955,092 (Apr. 17, 1934); L. Lilienfeld, U. S. Patent 1,658,607 (Feb. 7, 1928); H. Plauson, Brit. Patent 184,533 (Apr. 11, 1911); A. J. Hailwood, Brit. Patent 281,117 (Nov. 30, 1926); I. G. Farbenindustrie Akt.-Ges., Brit. Patent 434,540 (Sept. 4, 1935); du Pont, Brit. Patent 463,056 (Mar. 19, 1937); Deutsche Gasglühlicht-Auer-Gesellschaft m.b.H., German Patent 413,511 (Oct. 1, 1921); W. Grötzinger, French Patent 823,836 (Jan. 27, 1938).

[9] The name xanthate is derived from the Greek word "xanthos," meaning yellow, in view of the yellow color of the cuprous salt of xanthic acid. It should be mentioned also that xanthic acid is really the ethyl ester of dithiocarbonic acid and therefore the term cellulose xanthate is a misnomer. The latter compound is not the cellulose ester of xanthic acid but of unsymmetrical dithiocarbonic acid. The name viscose originates from the viscous nature of the solution of cellulose xanthate in dilute sodium hydroxide solution.

and triacetate, the trixanthate does not form readily. In the commercial viscose reaction, for example, the average degree of xanthate substitution is of the order of one xanthate group per two glucose residues. However, higher degrees of substitution and even polyxanthates are possible under special conditions, and the preparation and study of these higher xanthates have permitted a better understanding of the viscose reaction.

If cellulose is treated with certain tetraalkylammonium hydroxide solutions,[11] it disperses completely instead of merely swelling, as when treated with sodium hydroxide solution. When these molecular solutions of cellulose are reacted with CS_2, compounds are formed which have been shown to be the salts of cellulose trixanthic acid corresponding to the particular organic base employed. The reaction depends upon complete dispersion of the cellulose which in turn depends upon the concentration and molecular weight of the organic base. With 3 to 4 *N* tetraethylammonium hydroxide at 0°C., for example, the reaction is:

$$(C_6H_7O_2(OH)_3)_n + 3n(C_2H_5)_4NOH + 3nCS_2 \longrightarrow (C_6H_7O_2[OCS_2N(C_2H_5)_4]_3)_n + 3nH_2O \quad (3)$$

The trixanthate formed gives a trixanthogen $([C_6H_7O_5(CS_2)_3]_2)_n$ upon oxidation with iodine. With tetramethylammonium hydroxide, however, dispersion does not occur, and the trixanthate is not obtained. Using other bases and under other conditions of concentration, dixanthates are formed which upon oxidation with iodine give the dixanthogen $([C_6H_8O_5(CS_2)_2]_2)_n$.

If cellulose is allowed to react with metallic sodium in liquid ammonia and the resulting trisodium derivative is treated with CS_2 under special conditions, a product corresponding to the trixanthate is formed.[12] Also, if sodium cellulose xanthate, as produced commercially with 30 to 40% CS_2 based on the cellulose in the alkali cellulose, is dissolved to form a normal viscose solution containing, for example, 7% cellulose and 6% NaOH, and this *dispersed* xanthate is treated with further quantities of CS_2, the reaction continues and higher degrees of substitution, that is, polyxanthates, result. By procedures of this type, products containing

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[10] H. Ost, *Ann.*, **382**, 340 (1911); R. Wolffenstein and E. Oeser, *Ber.*, **56B**, 785 (1923); *Kunstseide*, **7**, 2, 27, 74 (1925); R. Bernhardt, *Kunstseide*, **8**, 173 (1926); E. Heuser and M. Schuster, *Cellulosechem.*, **7**, 17 (1926); T. Lieser, *Ann.*, **464**, 43 (1928); *Cellulosechem.*, **10**, 156 (1929); E. Geiger, *Helv. Chim. Acta*, **13**, 281 (1930); S. Iwasaki, *J. Soc. Chem. Ind. Japan*, **35**, suppl. binding, 91, 92 (1932).

[11] T. Lieser, *Chem.-Ztg.*, **60**, 387 (1936); T. Lieser and E. Leckzyck, *Ann.*, **522**, 56 (1936); T. Lieser, *Kolloid-Z.*, **81**, 234 (1937); Röhm & Haas, Brit. Patent 439,806 (Dec. 9, 1935).

[12] P. C. Scherer and L. P. Gotsch, *Bull. Virginia Polytech. Inst.*, **32**, 11 (1939).

nearly two xanthate groups per glucose unit (γ-values[13] up to 180) have been obtained.[14]

Thus, it will be seen that the degree of xanthate substitution is in proportion to the dispersion of the reacting cellulose. When the cellulose is completely dissolved, and presumably all OH groups are made available for reaction, a stoichiometric compound, that is, a trixanthate, results. When dispersion is not complete, only the OH groups that are actually "available" undergo reaction.

In commercial xanthation, the reaction occurs between CS_2 and *swollen* cellulose, not *dispersed* cellulose, and all of the OH groups are not "available." That chemical reaction does occur, however, with conversion of some OH groups to xanthate groups, is established by the high temperature coefficient of the reaction and the fact that the reaction curve follows the equation of a unimolecular reaction.[7] To understand what happens, it should be remembered that attempts to produce a soluble xanthate using concentrations of NaOH much above or below 18% in steeping have been unsuccessful.[15] However, it is not the concentration of NaOH surrounding the soda cellulose which determines the solubility of the xanthate, but the composition of the soda cellulose crystallites.[14] With 18% NaOH, soda cellulose I is formed, and this compound must be considered the basis of the xanthate reaction. (The possibility that soda cellulose II can react with CS_2 to give a soluble product has not yet been settled.) It is significant that in soda cellulose I the ratio of cellulose to NaOH is $2C_6H_{10}O_5:1NaOH$,[16] which corresponds closely to the ratio of cellulose to carbon disulfide used in commercial practice, that is, $2C_6H_{10}O_5:1CS_2$. (This ratio is equivalent to 23.5% CS_2 based on the cellulose, which is in line with concentrations actually used if it is considered that only 75% of the total CS_2 added reacts with the cellulose (see p. 825).)

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[13] The γ-value is the number of xanthate groups per 100 glucose residues; see H. Fink, R. Stahn, and A. Matthes, *Angew. Chem.*, **47**, 602 (1934); N. V. Nederlandsche Kunstzijdefabriek, German Patent 421,506 (Jan. 18, 1922); L. Lilienfeld, Brit. Patent 212,865 (June 2, 1923).

[14] If *fibrous* soda cellulose is treated with excess CS_2, soda cellulose IV is formed; see W. Schramek and F. Küttner, *Kolloid-Beihefte*, **42**, 331 (1935).

[15] K. Atsuki, *Cellulose Ind.* (Tokyo), **7**, 207 (1931); A. Lottermoser, *Z. angew. Chem.*, **42**, 1151 (1929).

[16] For another interpretation see H. L. Bredée, *Kolloid-Z.*, **94**, 81 (1941). In this article the viewpoint is taken that all of the sodium in the alkali cellulose may be shown to be available for reaction if enough CS_2 is present, and that therefore the sodium in the micelle will have reacted at least to some extent in cases where less CS_2 is used. This point is considered above, in Section A of this chapter.

This does not mean that a stoichiometric compound of this composition is formed. Soluble xanthates have been produced with a ratio of cellulose to CS_2 of 2.5:1 (19% CS_2),[7] and it has been claimed that 16% CS_2, and even less, is sufficient.[17] Moreover, fractionation of viscose with salt solutions (see p. 832) shows the presence of xanthates of various degrees of substitution, precluding the existence of a definite chemical compound in the ordinary sense. Finally, x-ray investigations[14, 18, 19] show that there is no change in the cellulose lattice upon reaction of fibrous alkali cellulose with carbon disulfide for limited periods of time (although after 36 hrs. the alkali cellulose lines disappear). Soda cellulose I is always present in commercial xanthate to a considerable extent, and a fibrous xanthate of the usual degree of substitution is soluble only when the crystallized portion of the cellulose consists of soda cellulose I. This indicates strongly that carbon disulfide penetrates only into the amorphous region of the cellulose during xanthation as commercially practiced, and that xanthation occurs only in this region and possibly on the fringes of the crystallized portion of the cellulose. Since the crystalline and amorphous areas in cellulose exist in the proportion of approximately 1:1, (see Chapter III, A and C) the CS_2:cellulose ratio of about 1:2, which is normally employed, simply reflects the ratio of these areas.[16]

With regard to the position of the reactive OH group or groups, the idea that the primary OH group in the 6- position is most capable of undergoing the xanthation reaction was rejected some time ago in favor of the secondary OH group in the 2- position.[20] However, here again, x-ray evidence that only the OH groups in the amorphous areas or on the surface react, suggests the more probable hypothesis that xanthation does not occur uniformly on any specific OH group.[21]

The "primary" xanthate reaction in the viscose process thus involves chemical reaction, but the usual ratio of CS_2 to cellulose (1:2) does not signify a stoichiometric compound. It represents, rather, the ratio of the amorphous and crystalline areas present (or the ratio of the surface to the

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[17] A. J. Burette, French Patent 430,221 (May 22, 1911); L. Lilienfeld, U. S. Patent 1,658,607 (Feb. 7, 1928); see also E. Berl and J. Bitter, *Cellulosechem.*, **7**, 137 (1926); K. Hess, *Die Chemie der Zellulose*. Akademische Verlagsgesellschaft m.b.H., Leipzig, 1928, p. 326.

[18] K. Hess, *Cellulosechem.*, **13**, 84 (1932); W. Schramek, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 226 (1938).

[19] G. Centola, *Atti congr. intern. chima. Roma, 10th Congr.*, **4**, 117, 129, 138, 722, 728 (1938).

[20] T. Lieser, *Ann.*, **470**, 104 (1929); **483**, 132 (1930).

[21] T. Lieser, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 272 (1938).

interior of the micelles), the xanthate groups being distributed more or less haphazardly over the macromolecule. Since, in the reaction between cellulose and NaOH, the inherent energy is insufficient to overcome the lattice forces completely, the soda cellulose, after treatment with CS_2, probably dissolves in the intercrystalline, unoriented regions of the fiber only. That is, the crystallites remain intact and the CS_2 reacts only with those portions of the soda cellulose which are outside of the lattice. The reaction also involves swelling and physical dispersion of the cellulose, the soluble xanthated portions exerting a peptizing effect on the crystalline portions. The resulting compound is probably a mixture of cellulose molecules of varying chain length, substituted to varying degrees depending upon the accessibility of the OH groups to the CS_2. On this basis the formula for the xanthate may be written:

$$(C_6H_{10}O_5)_n\left[C_6H_7O_2(OH)_x(O{-}\underset{\underset{S}{\|}}{C}{-}SNa)_{3-x}\right]_m$$

in which the $C_6H_{10}O_5$ units within the parentheses are those groups which are in the crystalline portion of the cellulose (or within the interior of the micelle), while the expression in brackets shows those $C_6H_{10}O_5$ groups in the amorphous area and at the surface of the crystallites which have reacted with the carbon disulfide.[14, 18, 21]

In addition to the main reaction between alkali cellulose and carbon disulfide, side reactions also occur during xanthation. These are of two types: (1) secondary reactions of the xanthate itself and (2) direct reaction between carbon disulfide and free NaOH. The secondary reactions of the xanthate are brought about by its instability and the reversible nature of the reaction with carbon disulfide. The primary reaction (see equation (1)) should thus be written as an equilibrium reaction, which is forced to the right by increasing the concentration of CS_2. Secondary reactions of the following types also have been suggested:

$$R_{cell}{-}CS_2Na + 2NaOH \longrightarrow Na_2CO_2S + NaSH + \text{Cellulose} \quad (4)$$

$$R_{cell}{-}CS_2Na + NaSH \longrightarrow Na_2CS_3 + \text{Cellulose} \quad (5)$$

The thiocarbonate may further react with NaOH forming carbonate and hydrosulfide:

$$Na_2CO_2S + NaOH \longrightarrow Na_2CO_3 + NaSH \quad (6)$$

The other side reaction between CS_2 and NaOH may be expressed in the standard way:

$$3CS_2 + 6NaOH \longrightarrow 2Na_2CS_3 + Na_2CO_3 + 3H_2O \quad (7)$$

Regardless of the exact nature of these side reactions,[22] the secondary products consist of carbonate, trithiocarbonate, and probably hydrosulfide and sulfide. They are more stable than the primary xanthate and are responsible for the orange or carrot color of commercial xanthate and viscose. (Pure cellulose xanthate is practically colorless.) In the formation of the xanthate, an equilibrium is undoubtedly reached between it and the secondary products mentioned, although, because of the complicated nature of the mixture, it is difficult to determine satisfactorily the predominating equilibrium. Under normal industrial conditions, about 75% of the CS_2 used reacts with the cellulose and 25% appears as by-products in the *freshly prepared* viscose. (This excludes a small (5–10%) proportion of the CS_2 added which either does not react or is lost mechanically.) Thus, a *fresh* commercial viscose containing 7% cellulose and 2.0% total sulfur (equivalent to 34% CS_2 on the cellulose) normally shows the presence of about 1.5% xanthate sulfur.

Besides the conversion of OH groups to xanthate groups, colloidal changes occur during xanthation which are characterized by an extraordinary swelling (during which the form of the fiber is partially destroyed), by increased solubility (p. 824), and by a drop in viscosity. The latter is due to degradation of the cellulose, that is, a reduction in chain length, the extent of the degradation being dependent upon the time, temperature, and amount of oxygen present.

The solution of the cellulose xanthate in water or dilute caustic solution may be considered simply as a continuation of the swelling process which started with the formation of soda cellulose. From a colloidal standpoint it is essentially a peptization of a hydrophilic colloid. Complete solution is attained when the cohesive forces between the cellulose chains are overcome and the molecules become free to move in the solvent. The fiber bond is dissolved but not the soda cellulose crystallites. It has been variously suggested that true xanthate formation occurs only when the xanthation product is dissolved, that association[23] takes place during solution, and that NaOH or H_2O is combined chemically with conversion of the C = S group to $C\begin{<}^{OH}_{SNa}$ or $C\begin{<}^{OH}_{SH}$ However, x-ray data indicate there s no change in the cellulose lattice and no basis for believing that any new

[22] M. Ragg, *Chem.-Ztg.*, **32**, 630, 654, 677, 730 (1908); **34**, 82 (1910); H. Leuchs, *Kunstseide*, **7**, 286 (1925); G. Kita and R. Tomihisa, *Cellulose Ind.* (Tokyo), **2**, 26 1926); *Cellulosechem.*, **10**, 134 (1929).

[23] B. Rassow and W. Aehnelt, *Cellulosechem.*, **10**, 169 (1929).

chemical compound is produced.[14] Only soda cellulose I or cellulose hydrate (depending upon the conditions of coagulation) have been found in the solution.

The actual degree of dispersion of the xanthate after dissolving in dilute caustic solution is still open to question. In commercial viscoses, the solution is colloidal and probably of a micellar character, although there is some evidence that the colloidal particles have a macromolecular structure and that the cellulose, at least in part, is molecularly dispersed.[16, 24] The dispersion or solubility is influenced by practically every variable in the process, including type of cellulose, steeping, pressing, shredding, degree of xanthate substitution, mixing conditions, and viscose composition.

In addition to its effect on the dispersion of the cellulose, the composition of the viscose in cellulose and free NaOH also affects the rate of ripening, the viscosity, the regenerating characteristics (spinning, casting, etc.), and the properties of the regenerated product. Other factors being constant, rate of ripening, viscosity, and reciprocal filterability increase with increase in cellulose concentration or with decrease in free NaOH concentration. Spinning and film-casting properties depend on the ratio of cellulose to caustic as well as upon the absolute concentrations, and a proper balance must be maintained between these constituents and the composition of the coagulating medium used. In comparison, for example, with cellulose acetate, the optimum concentration of cellulose in viscose is relatively low, being in the range of 6 to 10%. Attempts to employ more highly concentrated solutions have been unsuccessful.

3. The Reactions of Viscose

Viscose is a sirupy, oily, orange- or carrot-colored solution, with a characteristic odor which is due, in part, to hydrogen sulfide and polysulfides. It may be regarded as an emulsoid, with cellulose xanthate the dispersed phase, and, as such, it possesses many interesting characteristics and undergoes various chemical and colloidal reactions.

(*a*) *Viscose Ripening*

One of the most important characteristics of viscose is its instability. From the previous discussion it will be clear that cellulose xanthate is unstable, decomposing immediately after formation, and that viscose is a complicated mixture of cellulose xanthate, caustic, carbon disulfide, and

[24] S. M. Lipatov and N. A. Krotova, *Melliand Textilber.*, **15**, 553 (1934); H. Staudinger, *Ber.*, **71B**, 1995 (1938).

compounds formed by the interaction of these materials. During the ripening of viscose, spontaneous decomposition of the xanthate continues and all of these materials undergo further reaction. These changes are both chemical and colloidal in nature.

Chemical Changes. The most important chemical change is the decomposition of the cellulose xanthate itself which results in the gradual splitting off of CS_2 and regeneration of the cellulose. As might be expected in the case of a substance made up of a strong base and a weak acid, the reaction is predominately a hydrolysis reaction,[10, 23, 25] with the formation of free cellulose xanthic acid and NaOH until an equilibrium is reached according to:

$$\frac{[\text{Sodium cellulose xanthate}]\,[H_2O]}{[\text{Xanthic acid}]\,[\text{NaOH}]} = K \qquad (8)$$

Since the free xanthic acid is also unstable, liberating CS_2, the reaction is forced to the right, and more and more xanthate is decomposed, until finally the regeneration of the cellulose is complete. The reactions may be represented by the following equations:

$$R_{cell}\text{—O—C(=S)—SNa} + H_2O \longrightarrow R_{cell}\text{—O—C(=S)—SH} + NaOH \qquad (9)$$

$$R_{cell}\text{—O—C(=S)—SH} + H_2O \longrightarrow HO\text{—C(=S)—SH} + \text{Cellulose} \qquad (10)$$

$$HO\text{—C(=S)—SH} \longrightarrow CS_2 + H_2O \qquad (11)$$

The same end-products result by saponification, which also occurs to a slight extent, being more perceptible as the caustic content of the viscose increases:

$$R_{cell}\text{—O—C(=S)—SNa} + H_2O \longrightarrow HO\text{—C(=S)—SNa} + \text{Cellulose} \qquad (12)$$

$$HO\text{—C(=S)—SNa} \longrightarrow CS_2 + NaOH \qquad (13)$$

This decomposition of the xanthate during ripening, as represented by the changes in xanthate sulfur content, is shown graphically in Figure 54.

[25] B. Rassow and M. Wadewitz, *J. prakt. Chem.*, **106**, 266 (1923); R. Bernhardt, *Kunstseide*, **7**, 193 (1925); **8**, 257, 314 (1926); J. Frenkel, *Cellulosechem.*, **9**, 25 (1928); W. Klauditz, *Papier-Fabr.*, **37**, Tech.-wiss. Tl., 251 (1939); W. Vieweg, *Papier-Fabr.*, **37**, Tech.-wiss. Tl., 269 (1939).

In practice, the hydrolysis is not allowed to proceed to completion. Thus, a 7% cellulose viscose for use in rayon, containing initially approximately 1.5% xanthate sulfur (2.0% total sulfur), is normally ripened until the xanthate sulfur content reaches 0.9 to 1.1%. This represents a change in

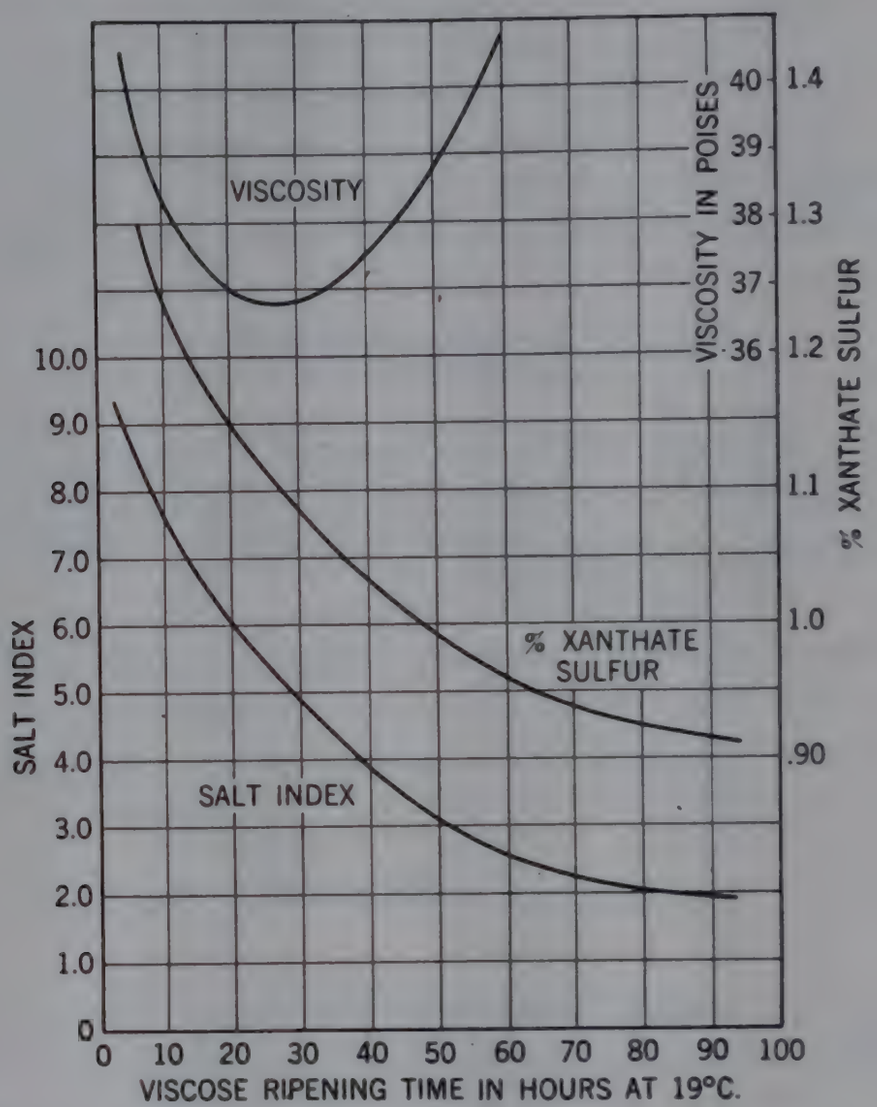

FIG. 54.—CHANGES IN SALT INDEX, XANTHATE SULFUR CONTENT, AND VISCOSITY DURING VISCOSE RIPENING.

Data are representative of a typical commercial viscose containing 7% cellulose, 6% NaOH, and 1.95% total sulfur.

the average degree of esterification from about $1CS_2:2C_6H_{10}O_5$ to $1CS_2:3C_6H_{10}O_5$. For many purposes, the viscose is used even before the xanthate sulfur has reached this range.

Besides the decomposition of the xanthate, other chemical changes occur during ripening, involving the secondary products. The formation of sodium trithiocarbonate and carbonate (p. 824) continues by reaction between NaOH and the CS_2 liberated from the free xanthic acid. Other

by-products include sodium sulfide, polysulfide, and thiosulfate. These side reactions have been variously represented, in addition to equation (7), as follows[10, 22, 26]:

$$5CS_2 + 12NaOH \longrightarrow Na_2S + 2Na_2CO_3 + 3Na_2CS_3 + 6H_2O \quad (14)$$

$$CS_2 + Na_2S \longrightarrow Na_2CS_3 \quad (15)$$

$$\left.\begin{aligned} Na_2CS_3 + 3H_2O &\longrightarrow Na_2CO_3 + 3H_2S \\ &\text{or} \\ Na_2CS_3 + 2H_2O &\longrightarrow H_2CS_3 + 2NaOH \\ H_2CS_3 &\longrightarrow H_2S + CS_2 \end{aligned}\right\} \quad (16)$$

$$Na_2CS_3 + 3NaOH \longrightarrow 3NaHS + Na_2CO_3 \quad (17)$$

$$CS_2 + 2NaHS \longrightarrow Na_2CS_3 + H_2S \quad (18)$$

The chemical changes may then be summarized by saying: In xanthation, sodium cellulose xanthate and by-product salts are formed side by side, with free CS_2 and NaOH remaining. After solution, new NaOH is added. Even though xanthate formation takes place more rapidly than the other reactions, the xanthate, being very unstable, is also decomposed faster than the secondary products. Xanthate sulfur content and free NaOH, therefore, decrease markedly, while the salt content increases. Several equilibriums are established until all the CS_2 has been converted and then a "salting out" effect sets in, due to the various salts present, which results eventually in precipitation of the cellulose as cellulose hydrate.[27]

Colloidal Changes. As an emulsoid, viscose shows many of the characteristic properties of a hydrophilic colloid, such as high viscosity, relative stability toward electrolytes, syneresis, weak electric charge, relatively great conductivity, etc., and during ripening some of these properties undergo significant changes. It has even been suggested that the colloidal processes predominate at first and induce the chemical changes,[28] although this seems doubtful.

The viscosity of viscose depends upon several factors, the more important of which are the degree of polymerization of the cellulose (determined by the type of cellulose, alkali cellulose aging conditions, etc.), the cellulose

[26] B. Rassow and K. Schwarze, *Papier-Fabr.*, **28**, Tech.-wiss. Tl., 746 (1930); H. Lotze, *Kunstseide*, **15**, 194 (1933); C. L. Moore, *Silk and Rayon*, **8**, 505, 563 (1934).

[27] There is some evidence indicating that the conversion of soda cellulose I to cellulose hydrate which occurs during ripening takes place by way of soda cellulose IV; see W. Schramek, *Kolloid-Beihefte*, **42**, 331 (1935).

[28] K. Atsuki, *J. Faculty Eng. Tokyo Imp. Univ.*, **17**, 135 (1927); *Cellulosechem.*, **9**, 106 (1928).

content, the degree of dispersion (alkali content and other factors influencing dispersion), temperature, and degree of ripening. The actual viscosity used in practice varies with different producers and with the nature of the product to be made. In addition to the requirements of the mechanics involved in transferring the solution through pipelines, in filtration, evacuation, spinning, casting, etc., there is an optimum viscosity for every combination of production factors (viscose composition, coagulating bath, speed of extrusion, etc.). From the standpoint of the strength and durability of the regenerated product, the use of a relatively high viscosity (high and uniform cellulose chain length) would seem desirable, but to date both mechanical and chemical difficulties have made it impossible to achieve optimum conditions in this respect. As a result, commercial viscoses range from 30 to 60 poises in viscosity, the weight-average degree of polymerization of the regenerated cellulose varying from about 250 to 600 glucose units.

As indicated above, viscosity is dependent upon degree of ripening, and one of the most peculiar colloidal changes during ripening is that involving the viscosity of the solution, which at first drops gradually, then passes through a minimum point, and finally rises slowly until coagulation is complete. This course of the viscosity change during the ripening of a representative commercial viscose is shown in Figure 54. The change in viscosity is not due to any change in the degree of polymerization of the cellulose. While some degradation of the cellulose occurs in every other step of the process, none occurs during ripening.[29] The initial drop in viscosity has been explained on the basis that solution of the xanthate is a slow process and requires time. While the xanthate apparently dissolves during the mixing operation, the dispersion is coarse and incomplete. Further solution, or disintegration of the cohesive crystallite groups, continues for 24 to 48 hrs. until the disintegration is complete, the viscosity decreasing as the dispersion approaches an optimum. In some cases the viscosity may actually rise slightly for a short time, before the drop just described. This rise is probably due to a further increase in the degree of hydration of the cellulose, and the decrease in viscosity may be simply the result of dehydration of the dispersed particles, that is, a decrease in the amount of water held by the internal dispersed phase due to osmosis.[28, 30]

The subsequent increase in viscosity is due to the opposite effect, that is,

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[29] E. Heuser and M. Schuster, *Cellulosechem.*, **7**, 17 (1926); S. Rogowin and M. Schlachover, *Cellulosechem.*, **14**, 17, 40 (1933); A. Lottermoser and F. Wultsch, *Kolloid-Z.*, **83**, 180 (1938).

[30] C. J. J. Fox, *J. Soc. Chem. Ind.*, **49**, 83T (1930).

desolvation. As hydrolysis proceeds, causing the ratio of combined sulfur to cellulose to become constantly smaller, the amount of regenerated, colloidally dispersed cellulose becomes constantly greater, and the degree of dispersion of the cellulose decreases due to association and aggregation, until visible coagulation sets in. The increase in viscosity which takes place is simply the manifestation of the decreasing dispersion and aggregation of the cellulose hydrate particles—a colloidal process independent of molecular size. Additional evidence of the colloidal nature of these changes is shown by the formation of structure during ripening,[31] and by the fact that the original viscosity may be restored (in fact, the whole ripening process may be reversed) by adding CS_2 to viscose at any stage of the process.

Viscosity is also dependent upon degree of dispersion, and hence the alkali content, of the viscose. While radical reduction in the viscosity of a viscose, after preparation, is not possible except by degrading the cellulose (indicating that the cellulose in viscose is partially in the form of a molecular dispersion), slight but important changes in viscosity can be produced by altering the caustic concentration (supporting the theory that the solution is of a micellar character). Increasing the NaOH content from 4 to 6%, for example, decreases the viscosity about 35%. The degree of dispersion, and hence stability, of viscose is greatest at a concentration of 8 to 9% free alkali; at this concentration it has the lowest content of hydration water and the viscosity is at a minimum.

Perhaps the most significant colloidal change in viscose during ripening is the change in its coagulation properties. As initially prepared, viscose is relatively stable and difficult to coagulate. Paralleling the chemical changes mentioned above, however, the solution coagulates spontaneously by virtue of the constantly decreasing solubility of the dispersed phase and increasing salt formation. Since the —CSSNa group is the solubilizing factor in the xanthate molecule (the cellulose itself is insoluble), as the number of —CSSNa groups per glucose unit decreases, the solubility of the material decreases. If these changes are allowed to proceed uninterruptedly and all the —CSSNa groups are split off, it becomes completely insoluble, and the solution is converted completely and spontaneously to a gel of hydrated cellulose. It is obvious that the rate of this change and the actual time required for gelation will vary considerably, depending upon such factors as temperature, the viscose composition, and the CS_2 content.

As spontaneous coagulation proceeds during ripening, the hydrophilic

[31] E. Berl and A. Lange, *Cellulosechem.*, **7**, 145 (1926).

character of the solution decreases and it becomes more and more hydrophobic in nature. This change is manifested by increasing instability and ease of coagulation with various agents such as acetic acid, alcohols, and inorganic salts. Being the salt of a stronger acid, the xanthate is not (readily) decomposed by monocarboxylic acids of the fatty series such as formic, acetic, and lactic acids, or by CO_2, SO_2, and other weak acids. (These acids do react with the free NaOH and decompose the by-product sodium salts with the formation of the sodium salts of the acid used and liberation of CS_2, H_2S, and CO_2.) Moreover, these acids do not usually coagulate freshly prepared viscose. As ripening proceeds, however, a point is reached where addition of an acid such as acetic also causes coagulation, and, as ripening continues, lesser and lesser amounts of acid are required for coagulation.

Methyl and ethyl alcohols, and alkali and ammonium salts, also coagulate viscose, precipitating the xanthate unchanged. In the case of the alcohols, the action is presumably due to simple dehydration. With inorganic salts, coagulation is based on a "salting-out" effect (dehydration of the dispersed phase) which follows an initial neutralization of the negatively charged xanthate particles by the first addition of the electrolyte. Whereas large amounts of alcohol and salts are required to coagulate the viscose when freshly prepared, lesser and lesser amounts are necessary as ripening progresses and the hydrophobic character of the solution increases. This change is shown by the salt index curve in Figure 54. At about 8 hrs.' ripening, an 8.0% NaCl solution is required for coagulation of a drop of this particular viscose. After 39 hrs., a 4.0% salt solution suffices, and after about 83 hrs. only a 2.0% solution is required (see p. 837). When 10% NH_4Cl is added to the same viscose solution, 27.2 cc., 10 cc., and 6.4 cc. are needed for coagulation after the respective ripening times.

Other changes during ripening include syneresis, increased turbidity, increased particle size, decreased dissociation, decreased conductivity, and changes in the light absorption bands.[32]

Control of Ripening. Since the spinning and casting properties of viscose as well as the quality and characteristics (tenacity, elongation, luster of filaments, clarity of films, dyeing, softness, etc.) of the end-product (rayon, cellophane) are determined in part by the degree of ripening, the normal instability of viscose is a major source of concern in its industrial

[32] T. Mukoyama, *Kolloid-Z.*, **41**, 62 (1927); **42**, 79, 180, 353 (1927); S. M. Lipatov, *Kolloid-Z.*, **49**, 441 (1929); R. Bernhardt, *Melliand Textilber.*, **7**, 55, 318 (1926); T. Sugita, *Cellulose Ind.* (Tokyo), **8**, 3, 166 (1932); R. O. Herzog, *Kolloid-Z.*, **35**, 193 (1924); Schwedler, Dissertation, Leipzig, 1927.

utilization. For this reason, precautions are taken to maintain constant conditions (constant salt index) and to inhibit or retard ripening. This is usually accomplished mechanically by such measures as the use of relatively low viscose temperatures (15–20°C.) during ripening, refrigeration and stepwise reduction in size of supply lines, and blending of batches (including the recirculation of viscose around the spinning machines and feed tanks). Chemical methods may also be used to retard ripening. It has been mentioned that the CS_2 and free alkali concentration influence ripening, the higher the content of these materials, the more stable the viscose and the slower the ripening. Other materials which have been proposed for addition to viscose to retard ripening include sodium sulfite, sodium cyanide, arsenites, certain urea and other amino derivatives, alkyl xanthates, phenols, calcium acetate, gallic acid, and others.[33] With the exception of sodium sulfite, however, none of these addition agents appears to be used in practice.

Consideration has been given also to methods for accelerating ripening in order to reach the desired degree of esterification more rapidly and thus to reduce or even eliminate the ripening step. It is obvious that this can be done in several ways, such as by raising the ripening temperature, by adding electrolytes, and by using low concentrations of NaOH and CS_2.[34] The addition to viscose of hemicellulose, polyalcohols like glycerol, and polysulfides and other materials[35] also accelerates ripening. While the effect of some of these agents is colloidal in nature, the action of most of the above-mentioned ripening accelerators and inhibitors is due to an actual change in rate of chemical decomposition of the xanthate.

(*b*) *Purification of Viscose*

Various suggestions have been made for the purification of viscose and the preparation of cellulose xanthate in a stable, dry form free from the

[33] C. A. Ernst, U. S. Patent 863,793 (Aug. 20, 1907); R. W. Maxwell, U. S. Patent 2,011,227 (Aug. 13, 1935); R. Linkmeyer and H. Hoyermann, German Patent 312,392 (Nov. 17, 1917); Lorch and Hammer, French Patent 728,682 (Dec. 21, 1931).

[34] C. A. Ernst, U. S. Patents 896,715 (Aug. 25, 1908); 863,793 (Aug. 20, 1907); Vereinigte Kunstseide-Fabriken Akt.-Ges., Brit. Patent 17,502 (Aug. 8, 1902); Société Française de la Viscose, Brit. Patent 8179 (1907); Soc. Anon. Soie de St. Chamond, Brit. Patents 1436 (Aug. 10, 1910); 24,291 (Dec. 18, 1914); Deutsche Zellstoff-Textilwerke, German Patents 339,050 (Oct. 12, 1918); 342,641 (Oct. 30, 1919); W. Mendel, German Patent 566,691 (Aug. 30, 1930); A. J. Burette, French Patent 430,221 (May 22, 1911).

[35] R. L. Cairncross and G. H. Goodell, U. S. Patent 1,814,543 (July 14, 1931); T. Mukoyama, *Kolloid-Z.*, **42**, 180 (1927).

usual by-product salts. Viscose can be coagulated with alcohol, salts, or a weak acid, or a combination of these agents, and the by-products can be removed by washing the precipitated xanthate with fresh precipitating solution. The washed xanthate may then be redissolved in caustic solution or dried if desired. Such procedures are of interest in studying the composition of the xanthate and viscose, since purified, dried xanthate is reasonably stable. Although a number of purification methods have been described and patented,[36] they are expensive, and they are superfluous so far as the major technical applications of viscose are concerned. They are, therefore, not used.

(*c*) *Additions to Viscose*

Besides the materials mentioned for controlling ripening, literally hundreds of others have been suggested or patented for addition to viscose for various purposes. These include solid and liquid, inorganic and organic compounds of almost every conceivable type, and they are added for almost every conceivable purpose, including improving or modifying the luster, dyeing, color, strength, elongation, softness, and other characteristics of the end-product, and the clarity, color, surface tension, viscosity, and spinning characteristics of the viscose. With the exception of those materials which are used for securing low luster (such as titanium dioxide and mineral oil), very few of the suggested additions to viscose find extensive practical use.

(*d*) *Analysis of Viscose*

A complete analysis of viscose includes the determination of the amount of cellulose, total alkali, total sulfur, viscosity, filterability, xanthate sulfur

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[36] L. Lilienfeld, U. S. Patent 980,648 (Jan. 3, 1911); Brit. Patent 14,339 (June 15, 1914); A. Bernstein, U. S. Patent 1,121,605 (Dec. 22, 1914); G. A. Richter and P. C. Scherer, U. S. Patent 1,880,041 (Sept. 27, 1932); H. B. Dykstra, U. S. Patent 2,072,738 (Mar. 2, 1937); Vereinigte Kunstseide-Fabriken Akt.-Ges., Brit. Patent 8742 (1908); H. Lyncke, Brit. Patent 8023 (1908); Viscose Syndicate Ltd., German Patent 133,144 (Mar. 31, 1901); Société Française de la Viscose, German Patent 187,369 (Aug. 13, 1904); Continentale Viscose Compagnie, German Patent 209,161 (Oct. 20, 1903); J. P. Bemberg Akt.-Ges., German Patent 197,086 (Mar. 29, 1907); F. Becker, German Patent 234,861 (Aug. 16, 1910); Deutsche Gasglühlicht-Auer-Ges., German Patent 408,822 (Apr. 29, 1922); R. Linkmeyer and H. Hoyermann, German Patent 312,392 (Nov. 17, 1917).

and/or xanthate soda (degree of ripeness or esterification by chemical tests), and degree of ripeness by coagulation tests.

The cellulose content of viscose may be determined readily by regeneration in the form of a film with salt solution or a mixture of salt and mineral acid. Total alkali is obtained by titration with sulfuric acid. Analysis for total sulfur is made by oxidizing the viscose with hypochlorite, hypobromite, or a mixture of hydrogen peroxide, nitric, and perchloric acids, and estimating it as barium sulfate. Filterability tests, which give considerable information as to the degree of dispersion, may be carried out by determining the rate of flow of viscose through a standard filter medium under standardized conditions of pressure, temperature, time, filter area, etc. Microscopic examination of the viscose, with dark-field illumination or under polarized light, also may be used to supply information on degree of dispersion.

Determination of viscosity is carried out using either the falling-ball or flow method. While the viscometers used are of the standard types, specifications regarding size of balls, tube and capillary diameters, and other dimensions vary considerably throughout the industry. To establish the "xanthate" viscosity of a pulp (or the viscose viscosity that will be obtained as the result of a given set of process conditions), it is necessary to convert the pulp to viscose under carefully controlled conditions. The small-scale laboratory procedure for the preparation of viscose described at the beginning of this chapter is satisfactory for this purpose.

Both chemical and colloidal methods are employed for determining the degree of ripeness or degree of esterification of viscose. Of the chemical methods, probably the best is the procedure based on the reaction of the xanthate with diethylchloroacetamide which converts it into an insoluble, stable derivative[13, 37] whose composition is:

$$\left(C_6H_7O_2[OH]_x[O-\overset{\overset{S}{\|}}{C}-S-CH_2-CO-N(C_2H_5)_2]_{3-x}\right)_n$$

After precipitation of this compound, it is filtered off, and the nitrogen is determined by the Kjeldahl method. Since every nitrogen atom corresponds to one xanthate group in the original sample, this procedure gives the degree of esterification of the cellulose, and the results may be converted to xanthate sulfur or xanthate soda.

The oldest chemical test for determining xanthate sulfur, xanthate soda

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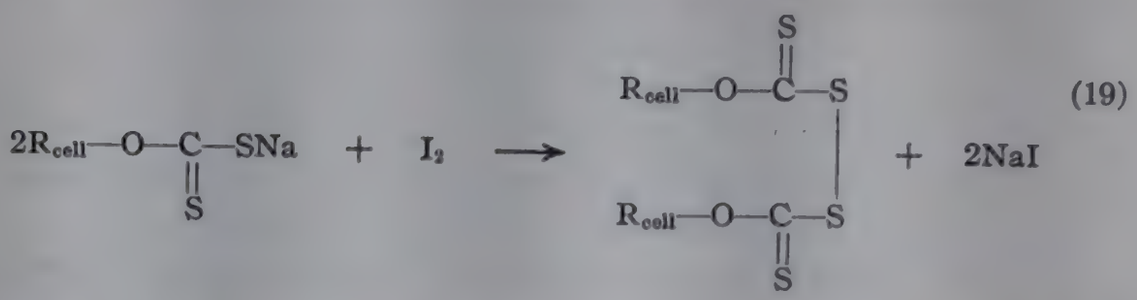
[37] H. Fink, *Angew. Chem.*, **47**, 429 (1934).

and degree of ripening is based on the reaction between cellulose xanthate and iodine which results in the formation of a so-called disulfide:



(19)

Because of the interference of the sulfur-containing by-products in viscose, this method is not as straightforward as the one using diethylchloroacetamide, and a number of variations in procedure have been suggested from time to time.[1, 7, 38] However, the method is used extensively and, with suitable precautions, reproducible results can be obtained which agree with the diethylchloroacetamide method. Perhaps the best and simplest procedure[39] is to remove the by-product sulfur compounds by treating the viscose with acetic acid in the presence of calcium carbonate which acts as a buffer, blowing with air (or, better, oxygen-free nitrogen), and then titrating with standard iodine solution. The change in xanthate sulfur content during ripening of a representative commercial viscose is shown in Figure 54.

The by-product sulfur content of viscose may be estimated by calculation as the difference between the total sulfur and xanthate sulfur contents. It may also be determined directly[39] by absorbing the CS_2 and H_2S, which are expelled as described in the above method for xanthate sulfur, in alcoholic NaOH and cadmium acetate solutions, respectively, and titrating with iodine.

Colloidal methods for determining the degree of esterification or ripeness of viscose are empirical in nature and measure the ease of coagulation rather than the amount of any chemical compound. They are more practical than chemical methods and they are also simpler. Two such methods are used extensively in industry as regular control methods. They

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[38] J. d'Ans and A. Jäger, *Kunstseide*, **8**, 17, 43, 57, 82, 110 (1926); *Cellulosechem.*, **16**, 22 (1935); H. Jentgen, *Laboratoriumsbuch für die Kunstseide- und Ersatzfaserstoff-Industrie.* W. Knapp, Halle (Salle), 1923, p. 55; O. Faust, E. Graumann, and E. Fischer, *Cellulosechem.*, **7**, 165 (1926); R. Bernhardt, *Kunstseide*, **8**, 164, (1926); J. Eggert, *Die Herstellung und Bearbeitung der Viscose unter bes. Berücks. d. Kunstseidefabrikation.* 2nd ed., J. Springer, Berlin, 1931; G. Kita, *Kunstseide*, **8**, 221 (1926); G. de Wyss, *Ind. Eng. Chem.*, **17**, 1043 (1925); H. Lotze, *Kunstseide*, **16**, 290 (1934); E. Berl and H. Dillenius, *Cellulosechem.*, **13**, 1 (1932).

[39] W. H. Fock, *Kunstseide*, **17**, 117 (1935).

involve the coagulation of viscose with sodium chloride and ammonium chloride solutions,[38, 40] and are based on the fact that with increasing age viscose may be coagulated by constantly smaller amounts of electrolytes.

1. The *Salt Point* or *Salt Index Method* gives the concentration of sodium chloride solution which is *just* sufficient to coagulate a definite, small quantity of viscose which is allowed to fall into it dropwise. There are several modifications of this test. One procedure is to allow one drop of viscose to fall from the end of a small glass rod ($^3/_{16}$ in. diameter) into a 250-cc. Erlenmeyer flask containing 40 cc. of salt solution of known concentration. The solution is immediately shaken mechanically for a definite period, and the salting-out effect is noted. If the drop of viscose dissolves, the salt solution is too dilute. If it coagulates as a heavy precipitate, the solution is too concentrated. At the correct concentration of NaCl, the drop forms two or three freely suspended, "comma-shaped" particles, readily seen by the naked eye.

2. The *Ammonium Chloride* or *Hottenroth Index Method* gives the volume in cc. of a 10% NH_4Cl solution which is necessary to coagulate the viscose under certain conditions. Viscose (20 g.) is diluted with 30 cc. of water and the solution titrated with 10% NH_4Cl solution, with rapid stirring, until coagulation just sets in.

It will be noted that in the salt index method a small quantity of viscose is added to a large volume of coagulating agent. The concentration and nature of the salt solution is therefore not appreciably affected. In the ammonium chloride method, the viscose solution is in excess. Moreover, the latter method depends upon the conversion of the ammonium chloride, first, by the free NaOH in the viscose forming sodium chloride and free ammonia, and, second, by the combined sodium, forming ammonium cellulose xanthate and more sodium chloride. The ammonium chloride method is, therefore, more sensitive than the salt index method and more dependent upon the composition of the viscose. The change in salt index during ripening of a representative commercial viscose is shown in Figure 54. It will be observed that there is a direct relationship between the salt index and xanthate sulfur curves, and hence between the colloidal and chemical methods for determining ripeness.

Other methods (both chemical and colloidal) for analyzing viscose have been suggested,[41] but for the most part they are not used extensively in industry.

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[40] K. Ziegler and W. Schäfer, *Cellulosechem.*, **15**, 89 (1934); V. Hottenroth, *Chem.-Ztg.*, **39**, 119 (1915); T. Mukoyama, *Kolloid-Z.*, **43**, 349 (1927).

[41] E. Berl and H. Dillenius, *Cellulosechem.*, **13**, 1 (1932); M. Numa, *Kunstseide*, **9**, 597 (1927); C. L. Moore, *Silk and Rayon*, **8**, 563 (1934). For the determination of impurities in viscose, which is often of great importance industrially, see E. Kühnel, *Kunstseide u. Zellwolle*, **21**, 369, 394 (1939).

(e) *Coagulation and Regeneration*

In view of the fact that viscose is of interest solely as an intermediate product from which the dissolved cellulose may be recovered in some desired physical form, its most important reaction is that by which the regeneration of the cellulose is brought about *rapidly*. The spontaneous decomposition of the xanthate during ripening obviously occurs too slowly to be of use industrially for this purpose, and the reaction with neutral salts results only in coagulation, with the xanthate remaining unchanged. Mineral acids and acid salts, however, decompose the xanthate *directly*, causing both coagulation and regeneration of the cellulose. At the same time, the free alkali is neutralized and the by-product salts are decomposed with liberation of CS_2, H_2S, CO_2, and free sulfur. The main reactions, as occurring with sulfuric acid, may be represented as follows:

$$2R_{cell}\text{—O—}\overset{\overset{S}{\|}}{C}\text{—SNa} + H_2SO_4 \longrightarrow 2R_{cell}\text{—OH} + Na_2SO_4 + 2CS_2 \qquad (20)$$

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O \qquad (21)$$

$$Na_2CS_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S + CS_2 \qquad (22)$$

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2 + H_2O \qquad (23)$$

$$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S \qquad (24)$$

If sodium sulfite is present in the viscose, liberation of H_2S is prevented and colloidal sulfur formed instead:

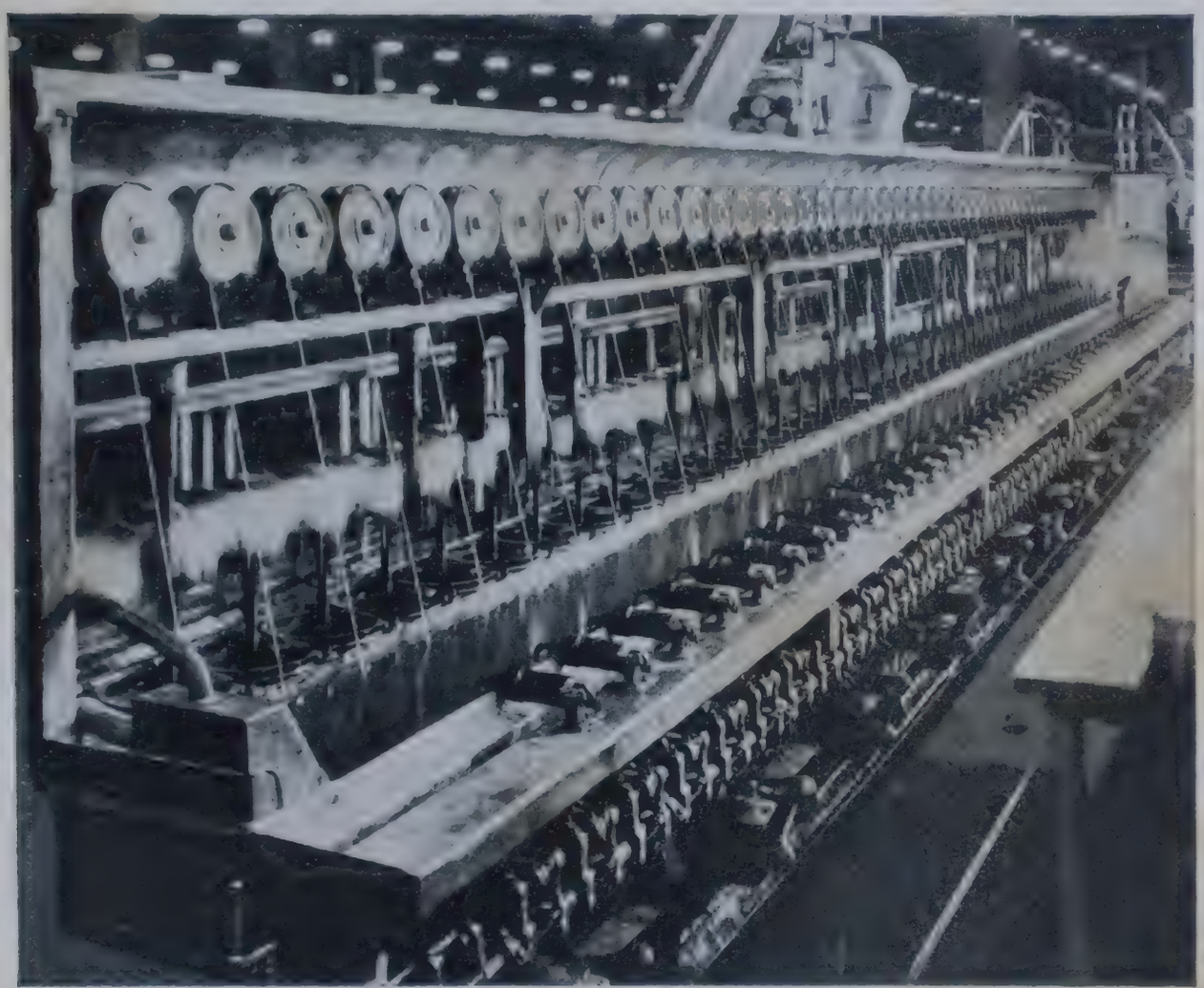
$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2 \qquad (25)$$

$$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S \qquad (26)$$

With few exceptions, these reactions, combined with the coagulation effect of neutral salts, are the basis of all industrial uses of viscose. The viscose is either extruded directly into a bath containing mineral acid plus one or more salts, causing immediate and simultaneous coagulation and regeneration, or it is first coagulated in a solution of one or more salts followed by regeneration in a second bath containing mineral acid. The former "one-bath" system is used most widely for the manufacture of filaments, while the latter "two-bath" system is employed mostly in the production of film structures.[42] Regardless of the regenerating methods employed, the cellulose is obtained as hydrated or mercerized cellulose, the characteristics of which have already been described in Chapter III.

[42] Dry spinning methods have also been suggested but they have not been applied industrially. See H. Hoffmann, *Papier-Fabr.*, **39**, 14 (1941); R. O. Herzog and H. Hoffmann, U. S. Patent 2,036,752 (Apr. 7, 1936).

Technical Applications. In the production of filaments (rayon and staple), the viscose is forced under pressure through very fine holes contained in cup-shaped nozzles (spinnerets) immersed in a coagulating bath. The emerging viscose filaments are coagulated immediately, and the coagulated fibers from each spinneret (each spinneret contains a



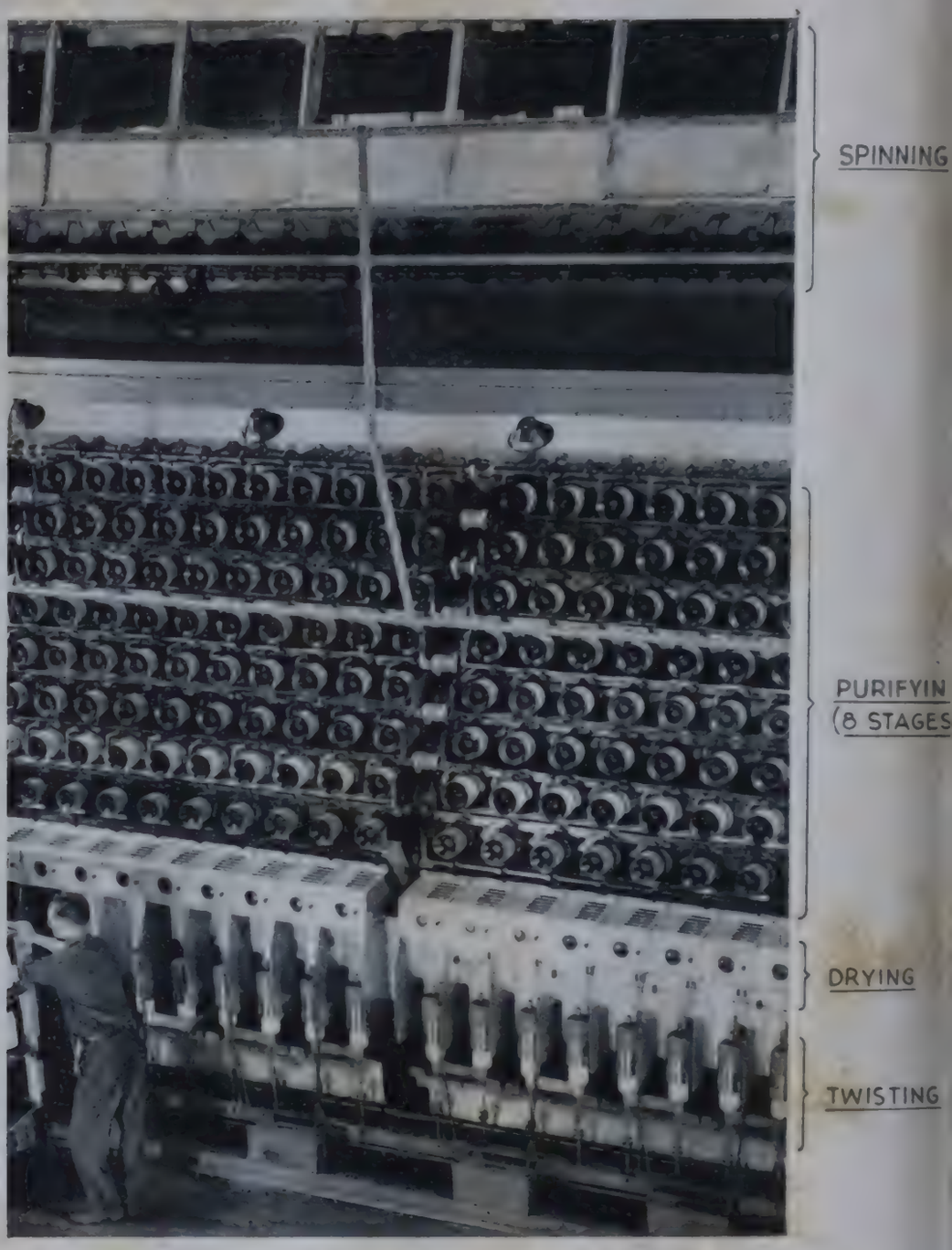
Courtesy of du Pont Co.

FIG. 55.—ONE TYPE OF "POT" SPINNING MACHINE.

The white lines up the face of the machine are the rayon threads as they leave the coagulating bath

number of holes) are combined into a main thread which is simultaneously drawn through the bath, stretched, and collected on a suitable take-up device (see Fig. 55). The size of the main thread, in the case of continuous filament rayon, varies from about 40 to 1100 denier, the number of filaments per thread varying from about 14 to 480. In the production of staple, the number of holes per spinneret is much greater, in some cases several

thousand, and the size of the main thread, per spinneret, may be as high as 10,000 denier or even higher.



Courtesy of Industrial Rayon Corp.

FIG. 56.—A "CONTINUOUS" SPINNING AND PROCESSING MACHINE.
This view shows how rayon is spun, purified, finished, dried, and twisted in synchronized operation.

Three methods are used in rayon production for collecting the freshly spun threads. They may be (1) wound on a rotating spool or bobbin, in the "spool" or "bobbin" process; or (2) collected in the form of a "cake" by centrifugal force in a revolving bucket, in the "bucket" or "pot" spin-

ning process (see Fig. 55); or (3) they may be wound on a specially designed rotating reel which receives and then advances the thread automatically and continuously (to a series of other similar reels for further processing), in the "continuous" spinning and purification process recently developed by the Industrial Rayon Corporation[43] (see Fig. 56). After spinning, and when regeneration of the cellulose is complete, the yarn is subjected to a number of operations, including washing, desulfuring, bleaching, finishing or oiling, drying, twisting, and winding to suitable packages (skeins, cones, etc.). These operations vary considerably throughout the industry, although in the "spool" and "pot" spinning processes they are all discontinuous. Each spool or cake, representing 0.50 to 2.0 lbs. of rayon, is treated individually as such, and the whole operation, from spinning to the final drying of the yarn, requires from one to six days. In the new Industrial Rayon Corporation "continuous" process, all of these operations except the final coning step are continuous; each thread is carried forward individually over a series of thread-advancing reels from the moment of extrusion until it is completely processed, dried, twisted, and wound on bobbins, and all of the operations are accomplished in about six minutes (see Fig. 56).

Excess coagulating bath is first removed from the freshly spun yarn by washing with water, sometimes in the presence of small amounts of an alkaline agent such as ammonia or sodium bicarbonate. In the "spool" and "pot" spinning processes, the yarn may be dried after this washing step, or further treated directly in the "gel" state (as is, or after reeling to skeins). Sulfur, which is always present, probably in both free and combined forms, is then removed by treatment with a dilute (0.5–1.5%) solution of sodium sulfide, ammonium sulfide, caustic soda, or sodium carbonate.[44] Other desulfuring agents have also been proposed.[45] When bleaching is required, it follows the desulfuring operation and is usually carried out with sodium hypochlorite solution[46] containing about 0.05% available chlorine. After

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[43] T. R. Olive, *Chem. & Met. Eng.*, **45**, 668 (1938).

[44] L. A. Paley, U. S. Patent 1,779,103 (Oct. 21, 1930); H. H. Parker, U. S. Patent 1,931,266 (Oct. 17, 1933); H. B. Kline, U. S. Patent 1,932,789 (Oct. 31, 1933).

[45] P. C. Scherer, *Ind. Eng. Chem.*, **25**, 1319 (1933); A. D. Conley and E. C. Stillwell, U. S. Patent 1,371,300 (Mar. 15, 1921); E. K. Gladding and T. S. Sharpe, U. S. Patent 1,655,097 (Jan. 3, 1928); A. Hartmann and J. Uytenbogaart, U. S. Patent 2,194,470 (Mar. 26, 1940); I. G. Farbenindustrie Akt.-Ges., Brit. Patent 279,437 (Oct. 14, 1927); A. E. Stein, Brit. Patents 428,955 (May 22, 1935); 429,165 (May 24, 1935); J. G. Evans, Brit. Patent 464,116 (Apr. 9, 1937); Herminghaus & Co., French Patent 655,729 (June 14, 1928).

[46] See also J. S. Fonda and G. W. Filson, U. S. Patent 2,064,300 (Dec. 15, 1936).

desulfuring and bleaching, the yarn may receive other treatments such as finishing, sizing, and tinting, after which it is dried. The latter operation is usually carried out without tension, and in such a way as to minimize shrinkage differences.

The manufacture of rayon staple resembles that of continuous filament rayon except that the main threads are much larger, as already pointed out, and the spinning and purification operations are nearly always continuous. Two main processes are in use, depending upon the cutting operation: (1) The filaments may be cut into staple immediately after spinning or washing and the remaining operations carried out on the cut fibers or (2) the thread or rope from a number of spinnerets may be combined and processed in rope form, after which it is cut to the desired length and then dried.

In the production of cellophane, viscose is forced under pressure (cast) through a slit in a suitable hopper which is immersed in a coagulating bath. As the viscose emerges from the slit, it is coagulated at once in the form of a thin, wide sheet or film. This is led by means of suitable rollers through a series of baths in which, after regeneration of the cellulose is complete, the film is washed, desulfured, bleached, etc., and finally dried. The entire operation is continuous, the machine being somewhat similar to, although much smaller than, a paper machine.

Sausage casings, bands, etc., are made by extruding viscose through an annular slot immersed in a suitable coagulating bath. The viscose is coagulated in the form of a tube, which is processed on a continuous machine through the various purification and drying steps.[47] Bottle caps, bands, etc., may be formed by covering suitable mandrels with a film of viscose by dipping, and then immersing in a coagulating medium. The viscose is thus regenerated as a film in the form of the particular mandrel used, after which the structure is removed from the mandrel and subjected to the necessary purification operations. Other cellulose structures are made from viscose in an analogous manner.

Coagulating Baths and the Spinning Operation. Since viscose is used most widely in the production of rayon and staple, its coagulation and regeneration are of concern mostly from the viewpoint of filament formation, that is, spinning.[48] In this connection, the composition of the coagulating bath is of prime importance. The bath serves several functions.

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[47] W. P. Cohoe, U. S. Patent 1,163,740 (Dec. 14, 1915).

[48] H. Erbring, *Kolloid-Beihefte*, **44**, 171 (1936); R. Klaus, *Kunstseide*, **15**, 9 (1933); **16**, 148 (1934); A. Wehrung, *Cellulosechem.*, **11**, 170 (1930); N. Matsumoto, *J. Soc. Chem. Ind. Japan*, **41**, B380 (1938); R. Inoue, *J. Soc. Chem. Ind. Japan*, **41**, B334, B357 (1938); **42**, B18 (1939).

It must coagulate the cellulose dispersed in the viscose and decompose the remaining xanthate; it must also neutralize the free alkali, decompose the by-product salts, and be compatible with the by-products of the reaction. Moreover, it must coagulate and regenerate the viscose as a homogeneous plastic mass, at a suitable speed so that the coagulated filaments may be readily and continuously led through the bath, stretched to a considerable extent if desired, and collected, all without interruption. These results have been achieved most satisfactorily by combining a reagent which actively decomposes the xanthate (dilute mineral acid) with an agent which simply coagulates (a salt).[49] The so-called Müller bath,[50] consisting of dilute sulfuric acid combined with a soluble sulfate salt, represents such a combination, and baths of this general type, although considerably modified, are in general use throughout the industry. The composition used is normally in the range of 7 to 13% H_2SO_4 and 13 to 25% Na_2SO_4. Magnesium sulfate, or ammonium sulfate,[51] is sometimes used in place of all or part of the Na_2SO_4. In addition, most coagulating baths today contain small amounts (0.5–1.5%) of $ZnSO_4$[52] and, in some cases, also organic materials like glucose,[53] and wetting or dispersing agents.[54]

Of the hundreds of reagents which have been studied for spinning baths, perhaps the most important are those in the class of inorganic salts. The coagulating effect of sodium and ammonium salts has been mentioned. Heavy-metal salts also react with viscose to give the corresponding metal xanthates, many of which are highly colored compounds.[1, 55] For example, the lead salt is carmine-red; the copper salt, chocolate-brown; the iron salt,

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[49] For some early bath compositions see: C. F. Cross, E. J. Bevan, and C. Beadle, U. S. Patent 604,206 (May 17, 1898); C. H. Stearn, U. S. Patents 622,087 (Mar. 28, 1899); 716,778 (Dec. 23, 1902); 725,016 (Apr. 7, 1903); Brit. Patent 2,529 (1902).

[50] F. Steimmig, *Kunstseide*, **12**, 242 (1930); M. Müller, U. S. Patent 836,452 (Nov. 20, 1906); Vereinigte Glanzstoff-Fabriken Akt.-Ges., German Patents 187,947 (Apr. 2, 1905); 287,955 (Feb. 15, 1912).

[51] T. H. Verhave, U. S. Patent 1,280,338 (Oct. 1, 1918); J. C. Hartogs, German Patent 324,433 (Mar. 1, 1914).

[52] S. S. Napper, U. S. Patent 1,045,731 (Nov. 26, 1912); F. C. Niederhauser and H. B. Kline, U. S. Patent 1,661,574 (Mar. 6, 1928); J. J. Stöckly and A. Brötz, U. S. Patent 2,015,201 (Sept. 24, 1935); Vereinigte Glanzstoff-Fabriken Akt.-Ges., German Patent 260,479 (Sept. 16, 1911).

[53] L. P. Wilson, U. S. Patent 970,589 (Sept. 20, 1910); E. Bronnert, U. S. Patent 1,426,953 (Aug. 22, 1922); Vereinigte Glanzstoff-Fabriken Akt.-Ges., German Patent 240,846 (Sept. 26, 1908).

[54] J. J. Polak and J. G. Weeldenburg, U. S. Patent 2,125,031 (July 26, 1938).

[55] H. Seidel, *Mitt. Tech. Gewerb.-Mus. Wien*, **10**, 35 (1900); R. Wolffenstein and E. Oeser, *Kunstseide*. **7**, 29 (1925); T. Lieser, *Cellulosechem.*, **10**, 156 (1929).

brownish red; the nickel salt, cherry-red; the zinc salt, white; the mercury salt, yellow; the cobalt salt, brownish black; the bismuth salt, red-brown; the cadmium salt, yellow; the silver salt, rose-brown; the antimony salt, red-yellow. Since solutions of pure xanthate do not give such intensely colored precipitates and since the compounds can also be obtained from the reaction products of CS_2 and NaOH, they are probably only in part cellulose xanthate salts. In any case, these and other metal salts also coagulate viscose, and since yarn properties (such as strength, elongation, dye affinity, luster, softness, and cross section) vary with the nature and concentration of the salt, many of them have become of definite interest as spinning bath constituents.

The action of salts is due in part to changes in *p*H,[21, 56] to changes in the speed of regeneration (which is reduced by the addition of salts[57]), and to the hydration of the ions. Most important, however, is the dehydrating, salting-out action which is common to all salts. In this connection the valence law of colloid chemistry and the Hofmeister series apply,[58] but only in part, in view of the hydrophilic character of viscose and the chemical reactions (mentioned above) which occur simultaneously. Thus, ammonium salts have a greater coagulating power than sodium salts, while the coagulating effect of divalent Mg^{++} is of the same order as monovalent Na^+, and heavy-metal salts like Zn^{++} are several hundred times more effective than either Na^+ or Mg^{++}.[59] The retardative influence on regeneration shown by these cations is in about the same order as their coagulating power,[60] and, when combined, their activity is nearly always greater than the sum of the individual salts.

These characteristics explain the use of various salts in baths and the special interest in zinc and other polyvalent cations, particularly in stretch-spinning processes to permit the application of tension, to increase strength, and to produce fine filament yarns. Being more soluble than Na_2SO_4, the use of $MgSO_4$ permits higher salt concentrations in the bath without crystallization difficulties, while $ZnSO_4$, even in the small concentrations mentioned above, deepens dyeing and improves strength, softness, and luster. Further very significant effects along these and other lines are

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[56] K. Tanemura, *Cellulose Ind.* (Tokyo), **11**, 12, 100 (1935).

[57] C. L. Moore, *Silk and Rayon*, **9**, 19 (1935); S. Hase, *J. Soc. Chem. Ind. Japan*, **35**, suppl. binding, 367 (1932).

[58] E. Berl and H. Dillenius, *Cellulosechem.*, **13**, 1 (1932); K. Leuchs, *Chem.-Ztg.*, **47**, 801 (1923).

[59] L. Mirlas, *Cellulosechem.*, **16**, 37 (1935).

[60] V. Duchesnoy, *Russa*, **9**, 641 (1934).

obtained by higher concentrations (2.5–30.0%) of $ZnSO_4$,[61] and other salts, including the sulfates[62] of aluminum, chromium, iron, arsenic, nickel, cobalt, and manganese, have been proposed for various specific purposes. Sodium bisulfite, sodium and ammonium phosphates, sodium borate, sodium thiosulfate, sodium and ammonium bicarbonates, sodium silicate, sodium salts of fatty acids, sodium benzene sulfonate, salts of certain organic bases, and others[63] have also been suggested for use.

The nature of the acid is important also.[64] While sulfuric acid is perhaps the only acid used commercially, others[65] have been proposed, such as acetic and other fatty acids, hydrochloric, nitric, benzenesulfonic, phosphoric, and arsenic acids.

Many organic compounds[66] have been investigated as constituents of spinning baths, but very few are actually used. For the most part, organic additions are of interest in influencing thread formation apart from coagulation and regeneration. The outstanding materials of this type are glucose and certain wetting or dispersing agents. Glucose is used rather widely in concentrations of 2 to 10%, mainly to prevent crystallization. It also suppresses the action of the acid and the oxidation of H_2S, and influences the continuity of spinning, softness, and other yarn properties.[53] Various wetting and dispersing agents are used in the bath (in concentra-

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[61] W. P. Dreaper, U. S. Patent 1,626,454 (Apr. 26, 1927); Brit. Patent 239,254 (May 2, 1924); R. Picard, U. S. Patent 1,831,030 (Nov. 10, 1931); I. P. Davis, U. S. Patent 2,114,915 (Apr. 19, 1938); J. H. Givens, H. W. Biddulph, and L. Rose, U. S. Patent 2,192,074 (Feb. 27, 1940).

[62] C. H. Stearn, U. S. Patent 725,016 (Apr. 7, 1903); J. C. Hartogs, U. S. Patent 1,573,062 (Feb. 16, 1926); I. P. Davis, U. S. Patent 2,114,915 (Apr. 19, 1938); C. H. Stearn and C. F. Topham, Brit. Patent 16,604 (July 28, 1903); H. Kizu and K. Kadowaki, *J. Soc. Chem. Ind. Japan*, **38**, suppl. binding, 195 (1935).

[63] C. N. Waite, U. S. Patents 759,332 (May 10, 1904); 816,404 (Mar. 27, 1906); C. A. Ernst, U. S. Patents 798,027 (Aug. 22, 1905); 792,888 (June 20, 1905); E. Bronnert, U. S. Patents 1,102,237 (July 7, 1914); 1,374,718 (Apr. 12, 1921); 1,376,672 (May 3, 1921); 1,387,882 (Aug. 16, 1921); C. F. Cross, U. S. Patent 1,538,689 (May 19, 1925); H. Chavassieu, U. S. Patent 2,034,711 (Mar. 24, 1936); S. Peessarer, Brit. Patent 16,583 (Aug. 15, 1905).

[64] Y. Kami and M. Nozaki, *Cellulose Ind.* (Tokyo), **5**, 117 (1929).

[65] C. A. Ernst, U. S. Patent 792,888 (June 20, 1905); C. H. Stearn, U. S. Patent 725,016 (Apr. 7, 1903); L. P. Wilson, U. S. Patent 970,589 (Sept. 20, 1910); E. Bronnert, U. S. Patents 1,102,237 (July 7, 1914); 1,376,672 (May 3, 1921); 1,464,805 (Aug. 14, 1923); J. C. Hartogs, U. S. Patent 1,534,382 (Apr. 21, 1925); L. Lilienfeld, U. S. Patent 1,881,740 (Oct. 11, 1932).

[66] C. A. Ernst, U. S. Patent 792,888 (June 20, 1905); M. T. Callimachi, U. S. Patent 1,449,380 (Mar. 27, 1923); F. C. Niederhauser and A. E. Sunderland, U. S. Patent 1,625,562 (Apr. 19, 1927).

tions of a few parts per million) in some plants to prevent or reduce the formation of deposits in the spinneret holes.[54] These deposits, representing insoluble by-products of the reaction between viscose and spinning bath, adversely affect the quality of the thread and the continuity of spinning. They may be controlled under ordinary conditions by proper attention to various spinning factors, but the production of very fine filament yarns and the use of higher spinning speeds and of certain bath compositions to permit high stretching have aggravated this condition in recent years, creating interest in new and novel methods of correction.

While coagulation and regeneration usually occur simultaneously, they do not occur at the same rate. The absolute concentrations and the ratio of acid and salts[57, 67] determine which of these reactions predominate and, in turn, the quality and characteristics of the final yarn. In this connection, the presence of various materials in small amounts as impurities, such as traces of metals, may have a profound effect on the spinning operation. The cross section of the filaments, which is indicative of many yarn properties, also varies characteristically with bath (and viscose) composition.[68] "High-swelling" baths, such as sulfuric acid alone, give a circular cross section, with a relatively smooth outline and little or no "skin." "Low-swelling" conditions, produced by high salt concentrations, etc., cause the initial formation of a semipermeable surface film or skin. As coagulation and regeneration progress, an exosmosis of water takes place from the interior to the exterior of the filament, causing a decrease in volume and, hence, a shrinkage of the surface film, and giving an irregular, crenulated cross section.[69]

Besides the chemical composition of the bath, a number of physical factors play important roles in the spinning operation. These include bath temperature, bath travel, spinneret composition, spinning speed, spinning tension, and stretch. All of these factors, including viscose and bath composition, are interdependent, so that it is nearly always impossible to change any one of them without also making compensating changes in others. Bath temperature is usually controlled in the range of 45 to 55°C. where one-bath systems are employed, and the bath travel may vary from about 10 in. to several hundred inches. Spinnerets are made mostly of

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[67] P. Martin, *Rusta-Rayonne*, **11**, 275 (1936); E. Bronnert, U. S. Patent 1,393,197 (Oct. 11, 1921), and other Bronnert patents; P. Thivet, *Rusta-Rayonne*, **11**, 401 (1936).

[68] E. Bronnert, *J. Soc. Dyers Colourists*, **38**, 153 (1922); R. O. Herzog, *Leipzig. Monatschr. Textile-Ind.*, **41**, 352 (1926); A. Jäger, *Kunstseide*, **13**, 325 (1931); P. A. Koch, *Klepzigs Textil.-Z.*, **40**, 17, 284 (1937).

[69] J. M. Preston, *J. Soc. Chem. Ind.*, **50**, 199T (1931).

precious metals, high platinum alloys being preferred. Spinning speed varies considerably, depending upon such factors as type of spinning machine, filament size, and bath composition. Most operations today employ speeds in the range of 3000 to 4000 in. per minute, although considerable attention is being given to faster operation.[70] Speeds up to 10,000 in. per minute and even higher are possible, although they involve radical changes from present practice.

The tension-stretch relationships during spinning are vitally important from the viewpoint of fiber properties. In the viscose, the cellulose crystallites or micelles are dispersed at random. In the spinning operation orientation occurs, and the degree of orientation determines the strength, elongation, dyeing, and other characteristics of the fiber. Some orientation of the crystallites on the outside of the filaments is brought about by surface friction, as the viscose passes through the spinneret holes. The major orienting effect, however, is accomplished by a draft or stretch imparted to the filaments due to the fact that the velocity of collection of the filaments is always greater than the extrusion.

The total stretch for any given yarn is governed by the spinneret hole diameter. (This varies with different producers and with the filament size from 0.0020 in., for the finest filaments, to about 0.0060 in. for the coarsest.) The *effect* of the stretch depends upon the stage at which it is applied. In the early methods of spinning "without tension" in which the thread passes directly from spinneret to collecting device, the stretch is imparted close to the spinneret. This gives little orientation, and the fibers are characterized by low tenacity and high elongation. Present methods, for the most part, involve so-called "tension spinning" or "stretch spinning" practices[71] in which stretching occurs relatively farther from the spinneret, that is, later in the coagulation-regeneration cycle. This is accomplished by interposing various mechanical "braking" devices[72] (such as fixed guides, freely rotating guides, and positively-driven rollers) between the spinneret and the final collecting device. While these stretching procedures are most commonly used in conjunction with baths of the Müller type, highest breaking strengths are obtained when they are combined with special

[70] H. Jentgen, *Kunstseide*, **19**, 261 (1937).

[71] O. Faust, *Kunstseide*, **14**, 362 (1932).

[72] C. A. Ernst, U. S. Patent 808,148 (Dec. 26, 1905); W. Harrison, U. S. Patent 1,930,803 (Oct. 17, 1933); H. Pfannenstiel and H. Meyer, U. S. Patent 1,933,999 (Nov. 7, 1933); F. H. Griffin, U. S. Patent 1,950,922 (Mar. 13, 1934); H. A. Schrenk, U. S. Patent 1,968,912 (Aug. 7, 1934); W. H. Bradshaw, U. S. Patent 2,012,984 (Sept. 3, 1935); W. H. Bradshaw and G. P. Hoff, U. S. Patents 2,083,251–2 (June 8, 1937); B. Borzykowski, Brit. Patent 149,295 (Aug. 31, 1917).

bath compositions such as strong (50–86%) sulfuric acid[73] (which imparts a simultaneous coagulating, swelling, and plasticizing effect) or with Müller-type baths followed by secondary baths or treatments, usually at higher temperatures.[74] By thus delaying the stretching, orientation of the interior of the filaments as well as of the surface occurs, and, hence, higher tenacity results. (The higher tenacity is obtained, however, at the expense of elongation.) Whereas the older spinning methods, "without tension," give breaking strengths of the order of 1.6 g. per denier (31,000 lbs. per sq. in.), "stretch-spinning" methods are now common which give 2.5 to 3.5 g. per denier, and, experimentally, strengths as high as 6.0 g. per denier (117,000 lbs. per sq. in.) have been obtained.

(f) *Further Reactions of Viscose*

Viscose undergoes several other reactions not mentioned in the previous discussion. For example, xanthic esters may be formed according to the general reaction:

$$R_{cell}\text{—O—}\overset{\overset{S}{\|}}{C}\text{—SNa} + X\text{—}R \longrightarrow R_{cell}\text{—O—}\overset{\overset{S}{\|}}{C}\text{—}SR + NaX \qquad (27)$$

in which R is an organic radical and X the negative ion of an inorganic acid. Thus methyl iodide forms methyl cellulose xanthate,[75] and diethyl sulfate forms ethyl cellulose xanthate. Both of these compounds are soluble in alkali and in certain organic solvents, and may be spun or formed into plastic masses.

When cellulose xanthate or viscose is allowed to react with halogen derivatives of polyvalent alcohols like α-dichlorohydrin, or with halogen derivatives of anhydrides of polyvalent alcohols such as epichlorohydrin, or with trithiocarbonic acid esters of polyvalent alcohols, one or more of

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[73] These baths have not been commercially satisfactory. See L. Lilienfeld, U. S. Patent 1,683,199 (Sept. 4, 1928), and other patents of Lilienfeld.

[74] H. C. Stuhlmann, U. S. Patent 1,901,007 (Mar. 14, 1933); A. Bernstein, U. S. Patent 1,996,989 (Apr. 9, 1935); I. P. Davis, U. S. Patent 2,114,915 (Apr. 19, 1938); J. H. Givens, H. W. Biddulph, and L. Rose, U. S. Patent 2,192,074 (Feb. 27, 1940); A. Hartmann and J. Uytenbogaart, U. S. Patent 2,194,470 (Mar. 26, 1940); Zellstoffabrik Waldhof and A. Bernstein, Brit. Patent 335,605 (June 27, 1929); Châtillon (Soc. anon. italiana per la seta artificiale), Brit. Patent 370,943 (Jan. 13, 1931); S. Riko, Y. Akizuki, and Y. Kikuti, *J. Soc. Chem. Ind. Japan*, **39**, suppl. binding, 31 (1936).

[75] L. Lilienfeld, U. S. Patent 1,680,224 (Aug. 7, 1928); Brit. Patent 252,654 (Oct. 18. 1926); German Patent 519,138 (May 30, 1926).

the OH groups of the cellulose is replaced[76] and compounds useful for spinning into filaments, etc., are produced.

With halogenated fatty acids, salts, and esters, viscose forms cellulose xantho fatty acid derivatives.[77] With monochloroacetic acid, for example, the reaction is:

$$R_{cell}—O—\overset{\overset{S}{\|}}{C}—SNa + ClCH_2COONa \longrightarrow \underset{\text{Sodium salt of cellulose xanthoacetic acid}}{R_{cell}—O—\overset{\overset{S}{\|}}{C}—S—CH_2COONa} + NaCl \quad (28)$$

The xantho fatty acid derivative thus formed may react further with ammonia, or with organic amines, such as aniline,[78] as follows:

$$R_{cell}—O—\overset{\overset{S}{\|}}{C}—S—CH_2COONa + C_6H_5NH_2 \longrightarrow \underset{\text{Cellulose xanthoanilide}}{R_{cell}—O—\overset{\overset{S}{\|}}{C}—NHC_6H_5} + \underset{\text{Sodium thioglycolate}}{CH_2(SH)COONa} \quad (29)$$

Cellulose phenylthiourethan

If the salt of the above thiourethan is now treated with an ester of an inorganic acid, such as ethyl iodide, the corresponding ethyl ester of cellulose phenylthiourethan results.[79]

Cellulose xanthate, itself, also reacts with organic amines[80] forming N-substituted thiourethans of the type:

$$R_{cell}—O—\overset{\overset{S}{\|}}{C}—NHR$$

while, if the cellulose xanthoacetic acid, mentioned above, is dissolved in methylaniline,[81] a salt, cellulose xanthoacetic acid amine, is formed:

$$R_{cell}—O—\overset{\overset{S}{\|}}{C}—SCH_2COOH \cdot HNC_6H_5(CH_3)$$

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[76] L. Lilienfeld, U. S. Patents 1,938,032 (Dec. 5, 1933); 2,004,876 (June 11, 1935); 2,021,862–4 (Nov. 19, 1935); see also L. Lilienfeld, Brit. Patents 335,906 (Mar. 25, 1929); 335,993–4 (Mar. 25, 1929); 356,286 (Mar. 10, 1930).

[77] T. Nakashima, *J. Soc. Chem. Ind. Japan*, **31**, suppl. binding, 31 (1928); L. Lilienfeld, U. S. Patent 1,642,587 (Sept. 13, 1927); Brit. Patents 231,800 (Nov. 23, 1925); 341,843 (June 20, 1929).

[78] L. Lilienfeld, U. S. Patents 1,674,401 (June 19, 1928); I,674,405 (June 19, 1928); 1,906,910 (May 2, 1933); Brit. Patent 231,802 (May 22, 1924).

[79] L. Lilienfeld, U. S. Patent 1,674,402 (June 19, 1928).

[80] L. Lilienfeld, U. S. Patent 1,881,741 (Oct. 11, 1932).

[81] L. Lilienfeld, U. S. Patent 1,890,393 (Dec. 6, 1932).

Xanthates of "oxy-(hydroxy-)alkyl" derivatives of cellulose are obtained by reacting cellulose with a cyclic ether of a polyhydric alcohol and then treating the resultant compound with carbon disulfide and alkali.[82]

Diazomethane converts the xanthate to monomethyl dicellulose:

$$[C_6H_7O_2(OH)_{2.5}(OCH_3)_{0.5}]_n$$

Diazonium compounds[83] also react with cellulose xanthate according to the equation:

$$R_{cell}\text{—O—}\overset{\overset{S}{\|}}{C}\text{—SNa} + ClN{=}NR \longrightarrow R_{cell}\text{—O—}\overset{\overset{S}{\|}}{C}\text{—SN}{=}NR + NaCl \longrightarrow \quad (30)$$

$$R_{cell}\text{—O—}\overset{\overset{S}{\|}}{C}\text{—SR} + N_2$$

in which R represents an aromatic nucleus such as C_6H_5.

The reaction of viscose with iodine has been described. The light-yellow disulfide formed here is insoluble and quite stable, although it is converted back to the normal cellulose xanthate by sodium amalgam.[20] Still other xanthates of cellulose, and other reactions of ordinary cellulose xanthate, as well as mixtures of cellulose xanthate and cellulose ethers, are possible.[84]

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[82] L. Lilienfeld, U. S. Patent 1,910,440 (May 23, 1933).

[83] J. H. Helberger, German Patent 562,180 (Oct. 1, 1931).

[84] L. Lilienfeld, U. S. Patents 2,051,051 (Aug. 18, 1936); 2,052,478 (Aug. 25, 1936); 2,100,010 (Nov. 23, 1937); 2,163,607 (June 27, 1939); 2,169,207 (Aug. 8, 1939); 2,176,085 (Oct. 17, 1939); 2,176,799 (Oct. 17, 1939).

Chapter IX

PHYSICAL PROPERTIES OF CELLULOSE AND ITS DERIVATIVES

A. SOLUBILITY

H. M. SPURLIN

In almost all of the industrial applications of relatively pure cellulose, with the exception of the paper and a portion of the textile industries, the ability of cellulose or its derivatives to be made fluid by the action of solvents, with or without the aid of heat, is the factor which makes their use possible. The interaction of cellulose and its derivatives with solvents and plasticizers has, therefore, been the subject of innumerable investigations. It is fortunate that within recent years the properties of solutions of high polymers such as cellulose have been almost entirely explained in terms of elemental chemical and physical concepts. The mathematical formulation of these relationships is reserved for Sections B and E of this chapter; the present discussion is limited to a general survey of the nature of the interactions of solvents with cellulose and its derivatives. In the first stages of this discussion, attention will be centered on the idealized cellulose molecule uncomplicated by the presence of ionizable bound metals and other factors promoting localized adhesion of chains, and then the effects of such impurities will be considered.

1. Characteristics of Cellulose Solutions

The phenomena involved are quite interesting, as they involve features not met with in the case of low-molecular-weight materials. The most characteristic behavior is the swelling which almost always precedes solution. The high viscosity even of dilute solutions is another outstanding property. Finally, such thermodynamic properties as freezing-point depression, boiling-point elevation, and osmotic pressure presented apparent inconsistencies which were not entirely explained until recently.

(*a*) *Analogies with Low-Molecular-Weight Compounds*

In order to gain a background for the understanding of these peculiarities of behavior, low-molecular-weight systems exhibiting similar properties

will be considered.[1] As a parallel for the swelling behavior of cellulose, the case of two immiscible liquids to which a third component, completely miscible in both phases, is added seems applicable. For example, if alcohol is added to a system composed of one part of water and ten parts of benzene, the water phase increases in volume much more rapidly than the benzene layer. As further quantities of alcohol are added, a point is reached where the two phases suddenly become miscible. Exactly the same type of behavior is noted if an active solvent such as acetone is added to a cellulose derivative suspended in a nonsolvent such as benzene; the cellulose-derivative phase increases in volume until a point is reached where, with a relatively small increase in the quantity of active solvent, the two phases become miscible in one another. The analogy in behavior between cellulose derivatives in the presence of poor solvents and systems with two liquid layers supports the view that cellulose derivatives are to be considered as liquids in their interaction with solvents. The underlying reason for this behavior will be referred to later in this paper and in Section B of this chapter. This viewpoint is confirmed by the evidence cited in Chapter III and in Chapter VIII, to the effect that the swelling observed with fibrous cellulose and its derivatives is confined almost entirely to the amorphous, and therefore essentially liquid, region. The minor increase in volume exhibited by the crystalline portion of the fiber is entirely analogous to that which occurs when an anhydrous salt unites with water to form a crystalline hydrate.

The viscosity of cellulose-derivative solutions is quite in accord with experience with low-molecular-weight compounds. For such compounds there is a quite regular increase in viscosity with molecular weight. It was as a result of studies of low-molecular-weight substances that Staudinger[2] arrived at his viscosity law, which states that the viscosity increment due to solution of a polymer is proportional to, or at least increases with, the chain length of the polymer.

Finally, as was pointed out by Kratky and Musil,[3, 4] the osmotic properties of cellulose-derivative solutions do not, on the average, depart to a

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[1] The work of J. H. Hildebrand (Am. Chem. Soc. *Monograph*, No. **17**, 2d ed., Reinhold, New York, 1936) furnishes a good basis for the consideration of solubility and miscibility of low-molecular-weight compounds. This work may be considered as the background for the viewpoint adopted in this section.

[2] H. Staudinger, *Die hochmolekularen organischen Verbindungen*. J. Springer, Berlin, 1932.

[3] O. Kratky and A. Musil, *Z. Elektrochem.*, **43**, 326 (1937).

[4] A. Musil, *Z. Elektrochem.*, **43**, 686 (1937).

reater extent from the laws of ideal solutions than do the solutions of nany low-molecular-weight substances of similar constitution when ompared at the same percentage by weight. The much greater im-portance of the deviations in the case of the polymeric materials is due to he fact that the osmotic properties themselves are so small. Further, it nust be remembered that, in addition to the heat effect due to interaction between solvent and solute considered by Kratky and Musil, a very considerable entropy of dilution, which causes deviations from Raoult's aw (see Section B of this chapter), exists in the case of polymers.

(*b*) *The State of Cellulose Derivatives in Solution*

It is clear that enough analogies exist with low-molecular-weight compounds of known structure to make plausible the supposition that solutions of long-chain molecules, such as those postulated for cellulose and its derivatives in Chapter II, would exhibit properties similar to those observed. The next step is to examine the evidence concerning the question of whether or not the solutions are actually molecular dispersions of large molecules. This question has been the origin of much discussion in the past. Experience with soaps and most inorganic colloids had familiarized chemists with the concept of dispersed particles consisting of aggregates of small molecules held together with van der Waals' or ionic forces, and there was a natural tendency to apply these findings to cellulose. One factor which should have warned against this procedure was the fact that colloidal solutions of the inorganic or soap types owe their distinctive properties to their electrical charges, while the characteristic cellulose derivatives, such as the acetate and the nitrate, are electrically almost neutral. In spite of this, the concept of micelles surviving in solution was widely held in the late 1920's and early 1930's. This concept varied from the assumption that the ultimate building unit consisted of a molecule containing only one or two glucose units to the assumption of relatively long cellulose chains held together side by side by means of secondary valence forces.

At present, however, all evidence supports the theory that molecular dispersions are possible, and that, in the absence of complicating factors, complete dispersion does take place. Because of the limitations of space, it is impossible to give a complete review of the three main theories of cellulose solutions, but the following summary of the more important points in each will give the reasons for the molecular dispersion viewpoint adopted in this book.

The three theories are these: (1) Each molecule is molecularly dis-

persed and only occasionally is associated with one of its neighbors. Any such association, if formed, is soon broken by thermal agitation. This theory, originally supported mainly by Staudinger,[2] has, as mentioned above, won almost universal acceptance. (2) The molecules are assumed to be grouped in bundles or micelles. There are two variations of this theory. In (a), usually ascribed to Meyer and Mark,[5] the micelles are assumed to be preformed in the substance and to maintain their individuality throughout the lifetime of the solution; if, by some chance attack, one of these micelles should be broken down into fragments, these fragments would not reassociate to form larger micelles. In (b), the micelles are supposed to be more stable in concentrated solutions than in dilute, but to have a relatively long life.[6] This theory has been of interest chiefly as a refuge for those who were convinced of the reality of Staudinger's results with very dilute solutions but were persuaded on *a priori* grounds of the probability of micelles in concentrated solutions. Of course, experience with soaps had some influence on this theory as well as on (3), in which it is assumed that the substances now known to be high-molecular-weight polymers are associated complexes of low-molecular-weight molecules[7, 8] held together by van der Waals' forces, hydrogen bonding, dipole interaction, or some other unknown force peculiar to lyophilic colloids. This concept, based as it was on analogies with inorganic colloids and on interpretations advanced for early x-ray results, was never taken very seriously by most of those actually engaged in the technology of cellulose. The foundations for this last concept were utterly removed when the structure of cellulose was established, so that it need be treated no further. Indeed, the main supporters of both theories (2) and (3) have now expressed agreement with Staudinger's views.[9, 10] The arguments against the existence of micelles in most solutions will, however, be outlined.

In this connection it must be pointed out that nothing is hereby implied about the existence of micelles in native fibers. There is undoubtedly in this case some sort of crystalline arrangement. There is also some evidence

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[5] K. H. Meyer and H. Mark, *Aufbau der hochpolymeren organischen Naturstoffe*. Akademische Verlagsgesellschaft m. b. H., Leipzig, 1930.

[6] K. H. Meyer and A. van der Wyk, *Helv. Chim. Acta*, **20**, 1321 (1937).

[7] K. Hess, *Die Chemie der Zellulose und ihrer Begleiter*. Akademische Verlagsgesellschaft m. b. H., Leipzig, 1928.

[8] R. O. Herzog and D. Krüger, *J. Phys. Chem.*, **33**, 179 (1929).

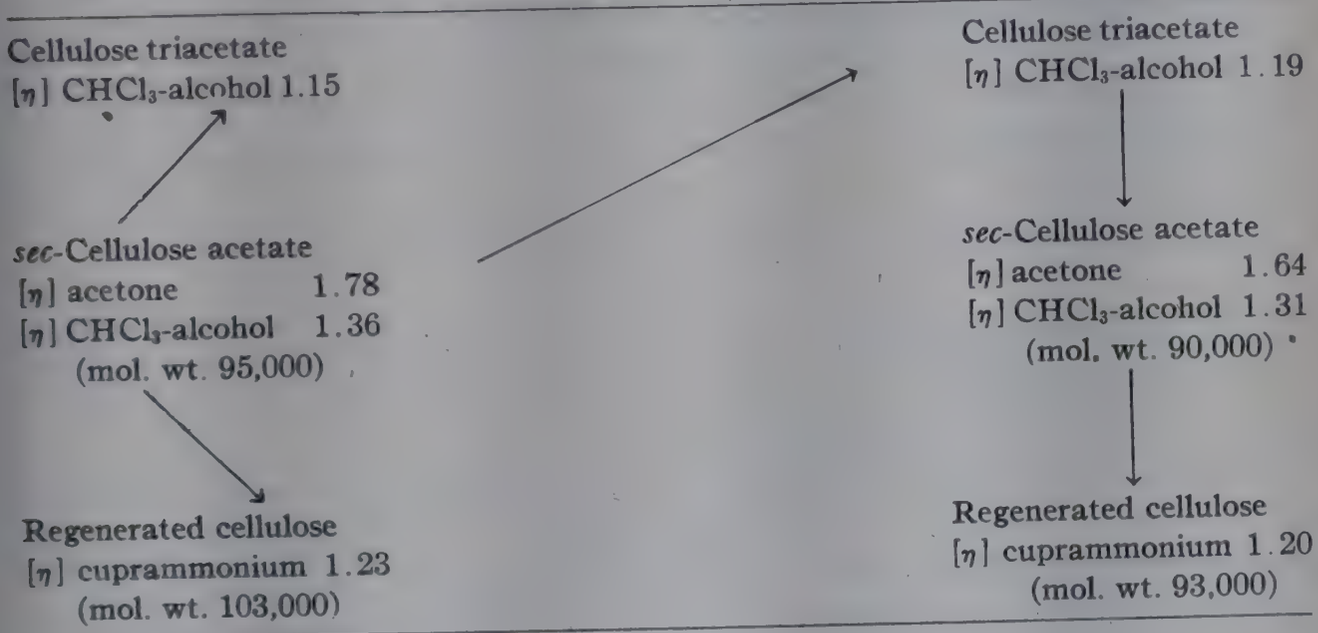
[9] K. H. Meyer, *High Polymers*, Vol. IV, *Natural and Synthetic High Polymers*. Interscience, New York, 1942.

[10] K. Hess and K. P. Jung, *Ber.*, **73B**, 980 (1940).

of ester[11, 12] or other linkages originally holding the cellulose chains together. In certain cases remnants of the fiber structure remain undispersed in what is sometimes referred to as a solution. Such remnants are always evident on ultramicroscopic examination and may be removed by filtration, leaving an optically empty solution. The most notable example of undispersed remnants of fiber structure in ordinary practice is encountered in a viscose solution prepared from fibrous cellulose xanthate which has not had opportunity for equalization of substitution throughout

TABLE 1

INTERCONVERSION OF CELLULOSE AND CELLULOSE ACETATE (KRAEMER[14])



the fiber structure (see Chapter VIII, A and F). The present discussion is not concerned with products similar to this, in which the average degree of substitution varies from chain to chain and even for different portions of the same chain, but rather with products which are essentially uniformly substituted.

The best argument against the existence of permanent micelles in solution lies in the ready conversion by chemical reaction of one derivative into another of the same degree of polymerization.[13] Tables 1 and 2 give pertinent data. It is certain in these cases, especially when the derivative is trisubstituted, that all of the cellulose chains have reacted. This seems

[11] H. Staudinger and R. Mohr, *J. prakt. Chem.*, **158**, 233 (1941).
[12] A. af Ekenstam, *Über die Celluloselösungen in Mineralsäuren.* Bloms, Lund, 1936.
[13] E. O. Kraemer, *J. Franklin Inst.*, **230**, 664 (1940).
[14] E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938)

incompatible with the continuing existence of micellar structure. Since the same degree of polymerization existed after the reaction as before, it would be necessary to assume some sort of memory which would enable the original micelles to reform with the same size.[15]

The kinetic studies which played such a role in establishing the structure of cellulose[12, 16] have shown quite conclusively that there is a perfectly uniform series of degradation reactions from the high-molecular-weight materials to monomeric glucose. The latter, as well as cellobiose, cellotriose, and other polymers of glucose, are known to be molecularly dis-

TABLE 2

CONVERSION OF CELLULOSE TO CELLULOSE NITRATE OF THE SAME MOLECULAR WEIGHT (STAUDINGER AND MOHR[11])

D.P. of cellulose (in cuprammonium solution)	76	152	186	210	254	336	356	450	480	720	1540	2000	2100	2550
D.P. of cellulose nitrate (in acetone)	77	135	170	180	220	310	330	440	460	670	1350	1800	2050	2301

persed. The question which then confronts the proponents of the micellar theory, and which they have failed to answer, is just where in the degradation series do micellar solutions first appear.

Similar to the arguments based on the transformation of one derivative to another are those based on the behavior of different solvents. It is known from a variety of effects, such as the x-ray studies of nitrocellulose-acetone gels,[17, 18] the optical rotation of cellulose in cuprammonium hydroxide,[19, 20, 21] the titration curves of derivatives containing acid groups, and studies of the thermodynamic properties of solutions (see Section B of this chapter), that there is interaction or combination of the solvent with the cellulose or derivative. The extent of this interaction is independent of the molecular weight. This can be explained only if each and every glucose unit is available for interaction with the solvent independently of all others. This would imply that the micelles, if they exist, react through and through with the solvent. Such behavior is incom-

[15] H. Staudinger, *J. prakt. Chem.*, **156**, 11 (1940).

[16] K. Freudenberg and G. Blomqvist, *Ber.*, **68B**, 2070 (1935).

[17] M. Mathieu, *Theories Chimique*, XIII, *La Gelatinisation des Nitrocelluloses. Actualités Scientifiques et Industrielles*, No. 317, Hermann & Cie., Paris, 1936.

[18] T. Petitpas, *J. chim. phys.*, **37**, 6 (1940).

[19] K. Hess and E. Messmer, *Ann.*, **435**, 7 (1923); *Kolloid-Z.*, **36**, 260 (1925).

[20] K. Hess, E. Messmer, and N. Ljubitsch, *Ann.*, **444**, 315 (1925).

[21] J. Compton, *J. Am. Chem. Soc.*, **60**, 1807 (1938).

patible with the idea that there are strong forces holding the micelles together. If strong forces do not exist, the micelles must dissociate in dilute solution, in the same manner as soap micelles.

The behavior of cellulose derivatives on fractionation, to be treated in more detail later, strongly implies that the ultimate particles in solution are molecules. The derivatives may be separated, by use of partial solution or precipitation, into fractions which, on repeated fractionation, finally approach a state where they resist further fractionation. On mixing the fractions, a product identical in its behavior with the original sample is obtained. This shows that cellulose contains fractions of different nature (as shown below, this difference is one of molecular weight) which maintain their properties through a succession of precipitations and resolutions. This permanence would imply, if the particles were micelles, such strong forces holding the structure together that it would be impossible to understand the ready solvation and reaction of all the chains mentioned above.

Further evidence of the same type is given by the osmotic pressure in different solvents and at different temperatures,[22, 23] which shows that the derivative has the same molecular weight in dilute solution regardless of the nature of the solvent or of the temperature of measurement. (The evidence for this is given in Figure 7A, to be discussed later in this chapter.) This shows again that either the micelles are exceedingly permanent or else they dissociate completely in dilute solution.

A further excellent argument against the existence of micelles in any concentration is furnished by the optical behavior of the solutions. Micelles of the size customarily postulated would become evident in the ultramicroscope by the Tyndall effect, on systematic variation of the refractive index of the solvent. Support has been lent the micellar hypothesis by the admitted turbidity of many cellulose-derivative solutions. Yet it has been known for years that with technically satisfactory products this turbidity is associated with only a small percentage by weight of the material, and it can be removed, for example, by fractionating out the highest-molecular-weight portion.[24]

In unpublished experiments by the writer, it was possible to secure optically empty cuprammonium solutions of cellulose by filtration through

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[22] A. Dobry, *J. chim. phys.*, **32**, 50 (1935); *Bull. soc. chim.*, [5], **2**, 1882 (1935); *Kolloid-Z.*, **81**, 190 (1937).

[23] C. G. Boissonnas and K. H. Meyer, *Helv. Chim. Acta*, **20**, 783 (1937).

[24] A. M. Sookne, H. A. Rutherford, H. Mark, and M. Harris, *J. Research Natl. Bur. Standards*, **29**, 123 (1942).

a Jena No. 5 sintered glass filter. Only 2% by weight was removed by this process.

According to Kraemer,[25] the behavior of cellulose derivatives in the ultracentrifuge is entirely incompatible with the existence of any large portions of the material in the form of rapidly sedimenting particles, as micelles of necessity would be. This evidence is particularly important in connection with cuprammonium solutions of cellulose, for which case there have been repeated contentions that the cellulose is dispersed in the form of micelles[26] or larger particles.[21, 27]

Still another important argument against the presence of micelles in concentrated solutions is the fact mentioned elsewhere that concentrated solutions of high- and low-molecular-weight materials show the same osmotic pressure and vapor-pressure lowering, while they differ by many orders of magnitude in viscosity. This behavior has received an adequate explanation on the basis of molecular dispersion in solution and kinetic independence of different portions of the chain (see Section B of this chapter). This freedom of movement would be impossible in a micelle, and no plausible explanation of the facts has been given by those supporting the micellar hypothesis.

It seems to be characteristic of cellulose derivatives, as well as of other linear macromolecules which are known to be molecularly dispersed in solution, that a universal equation expresses to a remarkable degree the variation of the viscosity of their solutions with concentration (see Sections E and F of this chapter). If micelles were formed in concentrated solutions but not in dilute, a discontinuity of some sort would be expected at the point where micelle formation begins, and this point should not be at the same concentration with different types of substitution. A universal equation, then, could not hold. Exceptions to the general relationship are found, however, in the cases where the substituents on the chain have high specific interaction. In these cases, gelation may occur (see p. 872), or the viscosity of the solutions will be strongly dependent on the solvent (see p. 878). A further example of exceptional behavior is found in the case of derivatives with ionizable substituents (see p. 890).

There is a logical basis, supported by experiment, for rejecting the idea of micelle formation in concentrated solutions of nonionizing solutes. It would seem that if the specific interaction between two molecules is large

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[25] E. O. Kraemer and J. B. Nichols, in T. Svedberg and K. O. Pedersen, *The Ultracentrifuge*. Clarendon Press, Oxford, 1940, p. 421.

[26] T. Lieser, *Ber.*, **74B**, 708 (1941).

[27] W. K. Farr, *Contrib. Boyce Thompson Inst.*, **10**, 71 (1938).

nough to cause them to adhere to one another along their whole length, third molecule would have a greater chance of being attached, due to greater surface area of the aggregate, and successive ones would have an ever-increasing chance of adding, so that the only stable situation would be the separation of large particles. (In the case of soaps and other ionizing bodies, unlimited increase in size of the micelle is opposed by electrical forces; even here, there is a strong tendency for crystal formation and formation of a separate phase.) Actually this is what is observed: on progressively increasing the attraction between chains by addition of a diluent or by change of temperature, very little change is noted until a separate phase is formed. Up to this point, the same type of viscosity-concentration curve is observed as before, either in the case of many derivatives having slight hydrogen bonding or in the case where polar diluents, which prevent association due to hydrogen bonding, are used.[28] Beyond the point of initial separation of a new phase, the supernatant liquor has all of the characteristics of a normal solution, with no evidence of micelle formation. In the frequent case where the new phase is also liquid, it also behaves as a normal solution. Further discussion of this behavior will be found under fractionation, on p. 880.

(c) *Factors Influencing Solubility*

The connection between the composition, both of the cellulose derivative and of the solvent, and solvent power has attracted much attention because of its technical importance. There have been numerous attempts to characterize solvents by one or two constants, such as surface tension, dielectric constant, dipole moment, and refractive index, but only one rule has been very successful: like dissolves like. Before discussing some of the correlations that have been attempted, it appears wise to demonstrate the complexity of the problem of solvent power by examining it in the light of recent theoretical advances.

Flexibility of Chains. As will be demonstrated in Section B of this chapter, long-chain molecules exhibit in solution a type of variation of activity with concentration not encountered with small, rigid molecules of the type used in developing the classical theory of solutions. This behavior is such that the activities of the solute and the solvent approach that demanded by Raoult's law only at infinite dilution. At higher concentrations, the activities are much lower.

It has been shown (see Section B of this chapter) both theoretically and

[28] Note in this connection the fine work of A. Dobry (ref. 22, p. 859).

experimentally that this effect is largely due to the entropy of dilution of the long-chain molecules. The linear macromolecules can assume many more configurations in dilute solution than in concentrated, and the solvent molecules can assume many more positions in concentrated solutions than would be possible if the molecules were rigid. The net effect is that the long molecules lower the activity of the solvent by the amount calculated from their molecular weight only in extremely dilute solutions (5×10^{-6} M or less (see Fig. 4, Section B of this chapter)). In concentrated solutions, the lowering of solvent activity indicates an apparent molecular weight of 400 to 1000, depending on the nature of the units of which the polymer chain is built, but not upon the actual molecular weight of the polymer. At intermediate concentrations, the apparent molecular weight of the polymer lies between this and the true values.

The relatively large entropy effects result in a considerably greater tendency for flexible molecules to go completely into solution than that shown by rigid molecules. The flexibility of the molecules also leads to the possibility of only a portion of the molecule becoming detached from the solid in one operation, successive portions then following. The operation of solution of a flexible molecule may thus be pictured as being similar to removing a piece of adhesive tape by pulling at one end. Not all of the adhesion must be overcome at one time. This means that the activation energy for solution is small.

Of course, the free energy change corresponding to the solution process is determined by the entropy effect plus the heat effect of the solution process. At first sight, the heat effect might be thought to be independent of flexibility, as the end result is the removal of the entire chain from the solid to the solution phase. However, as has been repeatedly pointed out, the characteristic feature of long-chain polymers is the swelling that precedes solution.

Swelling is essentially solution of the solvent in the polymer phase. The flexibility of the chains allows solvent molecules to penetrate the structure, portions of the chains moving apart in order to allow this. Again, it is the entropy associated with this effect which furnishes the driving force. The consequence is, however, that the phase in equilibrium with a border-line solvent is highly swollen, the chains maintaining contact with one another along a portion of their length only. This swelling behavior seems to be universally true for cellulose and its derivatives, even if they are initially crystalline in nature. As conditions are changed, therefore, in the direction of increased solvent power, the last stage before complete miscibility is a highly swollen gel which exists in contact with

he supernatant phase. In this gel, the extent of interaction between chains is much less than in the dry, solvent-free substance, and only this limited force of interaction must be overcome in the final solution process.

It is quite likely that the extent and ease of swelling will be more influenced by the degree of internal flexibility of the chains than will the entropy of the chains in solution. Cellulose chains are definitely not as flexible as vinyl or rubber-like polymers, due to hindrance of rotation about the oxygen linking the glucose units. Polyvinyl alcohol has the same ratio of hydroxyls to carbon as cellulose, yet is quite soluble in water. The greater flexibility of the polyvinyl chain must be the explanation. That this is not the only factor operating in such cases is apparent from the example of starch, which is also water-soluble. This appears to be due to the highly branched nature of amylopectin, the major constituent of starch. This branching prevents close packing of the starch chains alongside one another, thereby decreasing the forces to be overcome on solution.

Even in the highly swollen state prior to solution, the forces acting between chains will be a function of chain length, and the tendency for chains to leave this phase will be an exponential function of the degree of polymerization. Chains for which the net attractive energy is much larger than RT will not tend to go into solution, even though their tendency to swell will be just as great as in the case of shorter chains. This matter is discussed in more detail below and in Section B, under fractionation. As will be shown, the usual cellulose product is a mixture of chains of greatly differing length. In any case of border-line solubility, the smaller chains will have a greater probability of escaping from the swollen phase into the solutions. As a consequence, the relative proportion of the material dissolving furnishes a good indication of the relative solvent power of two liquids.

Quantitative evaluation of a solvent by this means would necessitate knowledge of the molecular-weight distribution curves of the derivative as well as of the attractive energy per unit length of chain and the length of the kinetic unit in the chain. All of these factors are theoretically susceptible of measurement with some certainty, but the evaluation has not been carried out in a single case so far. Fractional solubility determinations have been chiefly useful, up to the present, in following changes in solubility with varying substitution. As in this case the attractive force between chains is a function not only of the degree of substitution but of the degree of solvation, such determinations usually have only an empirical interest, the solubility curve obtained varying in shape from solvent to solvent.

Crystallinity. In the preceding discussion, the influence of the state of the polymeric material on solubility was treated. It is now necessary to consider the influence of the state of the material in the entirely undispersed portion in contact with the solvent. In actual cases, it is necessary to consider crystalline and noncrystalline arrangements as the two extreme ends between which there is an infinite degree of gradation. Well-developed crystalline orientation is commonly encountered only in derivatives maintaining the original fiber structure. In this case, it is difficult to distinguish between the effects of crystallinity and of actual intermolecular chemical combination, such as through ester groups, characteristic of the original fiber structure but ordinarily destroyed in processing. As far as the actual arrangement of neighboring molecules with respect to one another is concerned, this is probably substantially the same in the crystalline and noncrystalline states. The difference is probably one of extent of contact; the crystalline arrangement permits contact of the chains along their whole length, while, in the noncrystalline state, some portions of the chains will not have their attractive forces satisfied.[29] This state of affairs, similar to the swelling due to chain flexibility, will result in higher solubility of the noncrystalline portion than of the crystalline portion. This behavior is actually observed, highly oriented or native fibers being less soluble than amorphous precipitates of the same composition.[30, 31]

Attraction between Chains. In the preceding portion of this section, little attention has been paid to the nature of the forces holding the cellulose chains together and opposing their tendency, due to thermal agitation, to wander around in solution independently of one another. It must be recognized that it is not the absolute magnitude of this force which determines solubility, but rather the difference in, first, free energy necessary to separate solute molecules from their neighbors and solvent molecules from other solvent molecules, and, second, free energy gained when solute molecules come in contact with solvent molecules.[32] The manner in which this net free energy depends on the structure of cellulose and its derivatives, as well as the action of solvents in influencing the attractive force between molecules, is worthy of examination.

It is now generally accepted that in cellulose itself the chain molecules

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[29] O. Kratky, *Kolloid-Z.*, **68**, 347 (1934).

[30] H. Staudinger and A. W. Sohn, *J. prakt. Chem.*, **155**, 177 (1940).

[31] T. Lieser, *Cellulosechem.*, **18**, 122 (1940).

[32] K. H. Meyer and A. van der Wyk, *Helv. Chim. Acta*, **20**, 1313 (1937).

re held to their neighbors by very strong forces due to hydrogen bonding[33] see Chapter III, A). There is no evidence that cellulose can be dis- ersed without substantially reducing the extent of this hydrogen bonding y chemical combination involving the hydroxyl groups. It is quite easy o visualize the action of ordinary chemical substitution, the usual sub- tituent such as ethyl, acetyl, or nitro having no hydroxyls to enter into

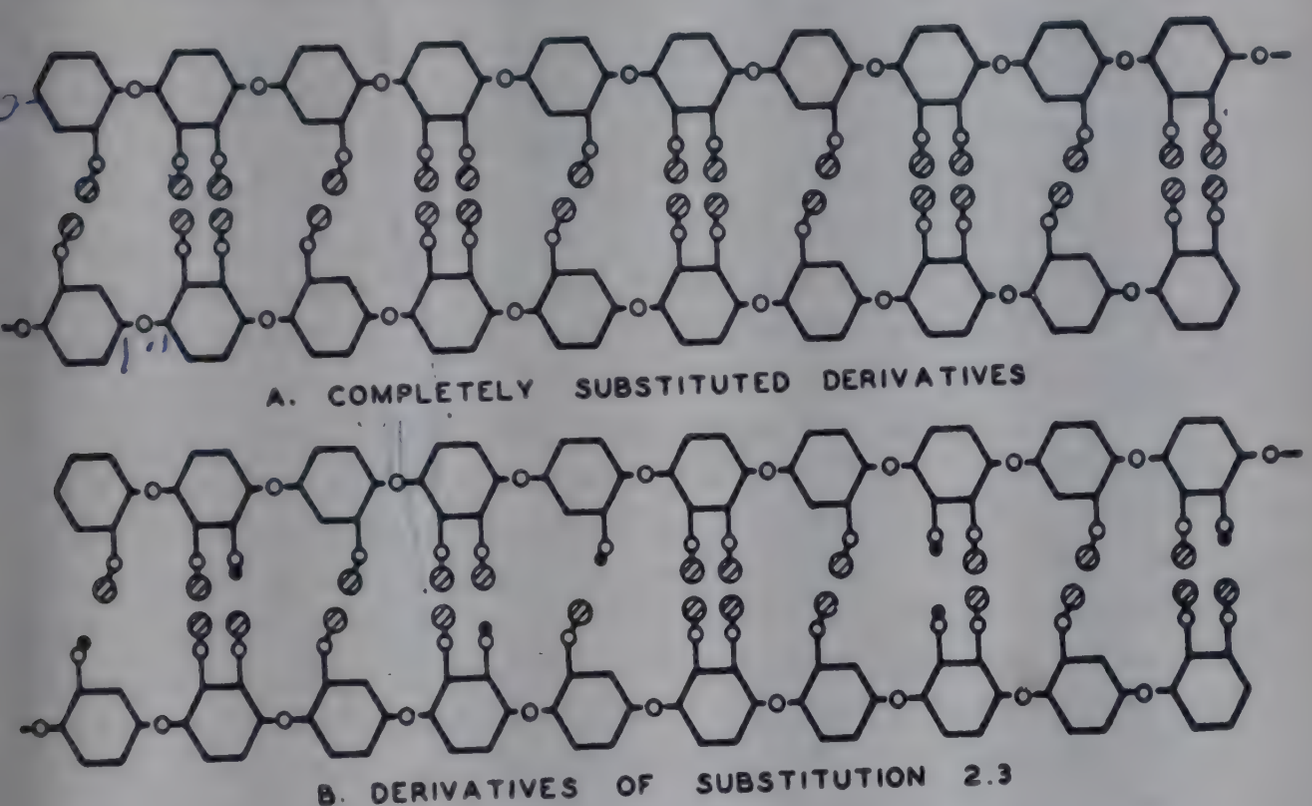

FIG. 1.—AREA OF CONTACT BETWEEN CELLULOSE CHAINS AND EFFECT OF SUBSTITUTION
Only substituents between chains are shown; oxygen atoms not shown in rings.

○—Oxygen.
●—Hydrogen.
⊘—Substituents.

hydrogen bonding. That hydrogen bonding is not the whole story is clearly shown by the maximum of solubility shown by all derivatives at some point short of trisubstitution (see Table 6, Chapter VIII, B, and Table 6, Chapter VIII, E). The explanation of this behavior is relatively simple. A completely substituted derivative has a very regular structure, enabling full contact with neighboring chains (Fig. 1, A). If a few sub- stituents are removed (Fig. 1, B), this regularity of structure is lost, and the total area of contact is much reduced. At the same time, as long as the number of hydroxyls is small, the chance of two hydroxyls being

[33] H. Mark, *High Polymers*, Vol. II, *Physical Chemistry of High Polymers*. Inter- science, New York, 1940.

opposite one another and being able to establish a strong hydrogen bond is small. This inability to establish hydrogen bonds will be more pronounced the larger the substituents are, so that, in this case, it may be necessary for several neighboring hydroxyls to be free on both adjoining chains before hydrogen bonding may occur, and the maximum of solubility will be found at a higher hydroxyl content than is the case with smaller substituents.

The influence of hydroxyls on the solubility of cellulose derivatives is of great technical importance. Cellulose triacetate is very difficult to dissolve, such solvents as methylene chloride or tetrachloroethane with a few per cent of alcohol being the only satisfactory solvents. This behavior serves to illustrate the very considerable magnitude of the forces between chains even in the absence of hydrogen bonding. If, however, enough of the acetyl groups are hydrolyzed off to leave a substitution of about 2.5, the solubility characteristics of the derivative are entirely changed. Acetone, alcohol-ester mixtures, acetic acid, and similar polar compounds are then the best solvents. The solubility in methylene chloride is, however, retained. As the substitution is further lowered, solvents of greater and greater polarity are required, until, at a substitution of approximately 1.0, the product is water-soluble but insoluble in organic solvents.[84] This behavior has caused attention to be centered on the action of the polar solvents on the hydroxyl groups, it being assumed that solvation is a prerequisite for solution. This is undoubtedly true in respect to derivatives of such high hydroxyl content that there is a large hydrogen bond interaction between chains. It is possible, however, to demonstrate that the main effect of introduction of a few hydroxyls in a trisubstituted derivative is to lower the attraction between chains. This follows from the fact that the softening point of the pure derivative is at a minimum at the identical substitution value where the solubility is at a maximum (Fig. 48, Chapter VIII, E). The softening point is, of course, influenced only by the forces between chains. Further, there is no *a priori* reason to suppose that solvation of a nonionized chain will promote solubility, except by reducing the attraction between chains.

Solvation.

Nature of Solvent-Solute Bonds. There is, fortunately, no necessity for introducing any new concepts when the influence of solvation is considered, as the solvation may be treated in the same manner as the formation of a

[84] C. R. Fordyce (to Eastman Kodak Co.), U. S. Patent 2,129,052 (Sept. 6, 1938).

new derivative by chemical action would be. The solvent molecule, if firmly enough held to justify the term solvation, is attached with sufficient strength to push the cellulose chains apart in quite the same manner as was postulated for the case of large substituents. Further, if the solvation occurs on a hydroxyl group, a potential source of hydrogen bonding between chains is removed. When a cellulose derivative dissolves, it is quite clear that the only forces tending to oppose solution are those between the solvated chains, and conclusions cannot be drawn from the relative hardness or high melting point of the unsolvated derivative.

The great influence of solvation on the force between chains is best exemplified by nitrocellulose, which in the pure state is quite hard and shows no sign of appreciable softening at elevated temperatures. In the presence of solvent plasticizers, which are simply high-boiling solvents, nitrocellulose compositions may be made quite soft and pliable. As was explained in Volume II of this series,[33] a soft, flexible state may be taken as evidence of low forces of attraction between chains.

The work of Mathieu[17] and Petitpas[18] illustrated quite well the close relationship between solvation, increase in distance between nitrocellulose chains, and decrease in attraction between chains. As the quantity of acetone, cyclopentanone, or methyl nitrate absorbed by the fibers increased, the distance between chains increased until one solvent molecule per C_6 unit had been taken up; beyond this point there seemed to be room for additional solvent molecules to be taken up in the structure without further lattice expansion. As soon as one solvent molecule per nitrate group had been taken up, the fiber structure entirely disappeared, showing that the attractive forces between chains had been sufficiently lowered for thermal agitation to disrupt the crystal structure; in other words, the crystal had melted. There is thus ample support in this work for the viewpoint advanced previously that the actual substance dissolving, in the case of the action of a solvent on a cellulose derivative, is not the hard, horny, high-melting solid represented by the material in a dry state, but rather a liquid of appreciable mobility.[35]

Unfortunately, the work of Mathieu and Petitpas cannot be taken as proving the existence of the stoichiometric 1:1 compound between solvent and C_6 units of nitrocellulose. The solvent absorption isotherms give no indication of a break at this point, and there is probably a very considerable difference between the solvent take-up of the amorphous and of the crystalline regions of nitrocellulose.

[35] See further in this connection S. Papkov, Z. Rogovin, and V. Kargin, *Acta Physicochim.* (*U.S.S.R.*), **8**, 647 (1938).

A further interesting sidelight to this work is furnished by the evidence that the solvent, particularly acetone, is bound only to the nitrate groups. This is, of course, very probable in any case, since trinitrocellulose is soluble in acetone, and since acetone is not a good solvent for cellulose derivatives containing much hydroxyl unless alcohols are also present. It is quite likely that chlorinated solvents are bound in a similar manner to the acetyl groups of cellulose acetate, rather than to the hydroxyls.

It is clear that, if the solvent molecules when forming solvates promote solubility by reducing the attractive forces between cellulose chains, the outer surface of the solvated chain must be changed in nature, the relatively strong attractive forces between polar groups and hydroxyls of the original derivative being replaced by weaker forces. A plausible explanation is that the most polar portions of the solvent molecules will be turned toward the polar groups of the cellulose chain, and the outer surface of the solvated chain will therefore consist of the nonpolar, hydrocarbon parts of the solvent molecule.[17, 36] In addition, it must be remembered that only a few solvent molecules can be bound to the cellulose chain, and these few will hold the chains apart, leaving gaps where no contact can occur.

In addition to the work of Mathieu and Petitpas already cited, there exists x-ray evidence for solvation, especially in the case of cellulose itself. Most of this evidence is reviewed in Chapter III, A. Cellulose itself forms definite compounds with acids, aqueous alkalies, and some organic bases, and possibly with water. Cellulose nitrate forms crystalline solvates with camphor,[37, 38] cyclohexanone, *p*-methylcyclohexanone, fenchone, and *m*-xylene,[39, 40] in addition to acetone, cyclopentanone, and methyl nitrate. Methyl nitrate and *m*-xylene, in spite of the fact that they form crystalline solvates, do not have the proper internal pressure to dissolve nitrocellulose.

Studies of the concentrations of acids most suitable for the pretreatment of cellulose prior to solution in stronger acids lend some support to the concept of definite crystalline complexes involving both acid and water.[12]

Just as conclusive evidence for the stability of solvates is the quite high heat effect observed when the first portions of solvent are added to a cellulose derivative, contrasted with the much smaller effect when the swollen

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[36] G. J. Esselen, *Ind. Eng. Chem.*, **12**, 801 (1920).
[37] K. Hess, T. Tomonari, and C. Trogus, *Z. physik. Chem.*, **B16**, 374 (1932).
[38] M. Wadano, K. Hess, and C. Trogus, *Z. physik. Chem.*, **B30**, 159, 183, 232 (1935).
[39] T. Tomonari, C. Trogus, and K. Hess, *Z. physik. Chem.*, **B17**, 241 (1932).
[40] C. Trogus, T. Tomonari, and K. Hess, *Z. physik. Chem.*, **B16**, 351 (1932).

derivative passes into solution.[41, 42] The preferential absorption of solvent by cellulose derivatives from dilute solutions of the solvent in an inert medium also demonstrates the strength of the bond uniting solvent to the cellulose derivative.[42] The conductivity of solutions of cellulose acetate and nitrocellulose containing added salts indicates a maximum of bound solvent molecules equal to four times the dry volume of the chain.[43]

There is thus ample evidence for strong forces holding solvent molecules to cellulose chains, and these comments on the similarity between the effects of solvation and of substitution by a large substituent are entirely in accordance with all of the evidence.

Points of Attachment of Solvent. Our present views on solvation were first clearly stated by Highfield,[44] who pointed out the importance of interaction between solvent molecules and specific portions of the cellulose molecule. For example, an alcohol has a great tendency to solvate hydroxyl groups, while, as stated above, methylene chloride seems to have a particular affinity for acetyl groups. A mixture of methylene chloride and an alcohol will thus have the ability to solvate both groups well. This alone would not be sufficient to dissolve the cellulose derivative, were it not for the fact that the field of force surrounding the molecules in the methylene chloride-alcohol mixture is similar enough to the field around the solvated cellulose-derivative molecules so that little difference in energy exists between the state of the chains in the undissolved and the dissolved states. It must be pointed out that there is considerable likelihood that this will be true in similar cases; the alcohol will be solvated by other alcohol molecules in the liquid state even though this union may be weaker than that to the cellulose hydroxyls. The nonpolar end of the molecule will thus always be turned outward in the solvent as well as in the case of the alcohol bound as solvate.[17, 36] The field of force around the methylene chloride molecules is probably not much altered by the relatively weak union with the acetyl groups, and the field of force around the portions of the chain solvated by methylene chloride will not be much different from that of methylene chloride itself.

The peculiar solvent properties of alcohol-ether mixtures have long attracted attention, the mixtures dissolving nitrocellulose of a degree of substitution which is unaffected by either component alone. Since the time

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[41] T. Nakashima and N. Saito, *J. Soc. Chem. Ind., Japan*, **38**, B232 (1935).

[42] T. A. Granskaya and A. I. Kaliteevskaya, *Colloid J. (U.S.S.R.)*, **6**, 145 (1940); *Chem. Abstracts*, **35**, 2715 (1941).

[43] A. Dobry, *J. chim. phys.*, **35**, 20 (1938).

[44] A. Highfield, *Trans. Faraday Soc.*, **22**, 57 (1926).

of Bernadou,[45] evidence has been available which makes it clear that the underlying phenomenon involved is solvation of the nitrocellulose by the alcohol, together with modification of the energy relations in the liquid by the ether,[36, 46] so that its resultant internal pressure is not too different from that of the solvated nitrocellulose. Ware and Bruner[47] also have pointed out the importance of solvation by the alcohol in explaining its activating influence in promoting the solvent power of ethers, halogenated hydrocarbons, esters, and aromatic hydrocarbons. Reduction of temperature greatly improves the solvent power of alcohol alone for nitrocellulose. This is undoubtedly due, to a considerable extent, to the greater stability of the solvate,[46] and also possibly to the different degree of association of the alcohol with itself, which will tend to reduce the internal pressure of the medium. This viewpoint bears some relationship to the theory of Byron,[48] who ascribed the solvent power of alcohol to the presence of polymers of alcohol.

Generalizations about Solvent Power and Other Properties of Solvents. Much effort has been expended in the search for some single function, be it based on physical properties or chemical composition, which will correlate adequately with the observed solvent powers of different substances. In view of the undoubted validity of Highfield's observations on the differences between the interactions of different portions of the substituted cellulose molecule with the solvent,[44] such a correlation is, in principle, impossible. Rather, it would be necessary to set up criteria for solvation of these individual portions, together with criteria for the internal pressure of the resulting solvate and for the medium.[1]

However, in view of the fact mentioned previously (p. 864) that there seems to be a tendency for the internal pressure of the solvated cellulose chain to approach automatically the internal pressure of the solvent, at least in the case of optimum mixtures of solvents, the most important factor becomes the ability to solvate the chain. The most useful generalization in this connection seems to be that the solvent must contain at least a minimum number per unit weight of those groups which have been found by experience to have a solvating action.[49] Such groups for nitrocellulose are: ester, carbonyl, amino, hydroxyl, carboxyl, sulfonamido, nitro, cyano,

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[45] J. B. Bernadou, *Smokeless Powder, Nitro-Cellulose, and Theory of the Cellulose Molecule.* 2d. ed., John Wiley, New York, 1908, preface.

[46] E. Berl and W. Koerber, *J. Am. Chem. Soc.*, **61**, 154 (1939).

[47] V. W. Ware and W. M. Bruner, *Ind. Eng. Chem.*, **32**, 519 (1940).

[48] M. L. Byron, *J. Phys. Chem.*, **30**, 1116 (1926).

[49] W. Coltof, *J. Oil Colour Chem. Assoc.*, **23**, 176 (1940).

and, in general, highly polar groups. Ether oxygens are less effective. A satisfactory solvent or solvent plasticizer for nitrocellulose must contain one or more ester or carbonyl groups for about 8 carbon atoms; for cellulose acetate, one such group for each 3 to 5 carbon atoms is desirable. Even in this case, true solvent power is not reached, although solvation

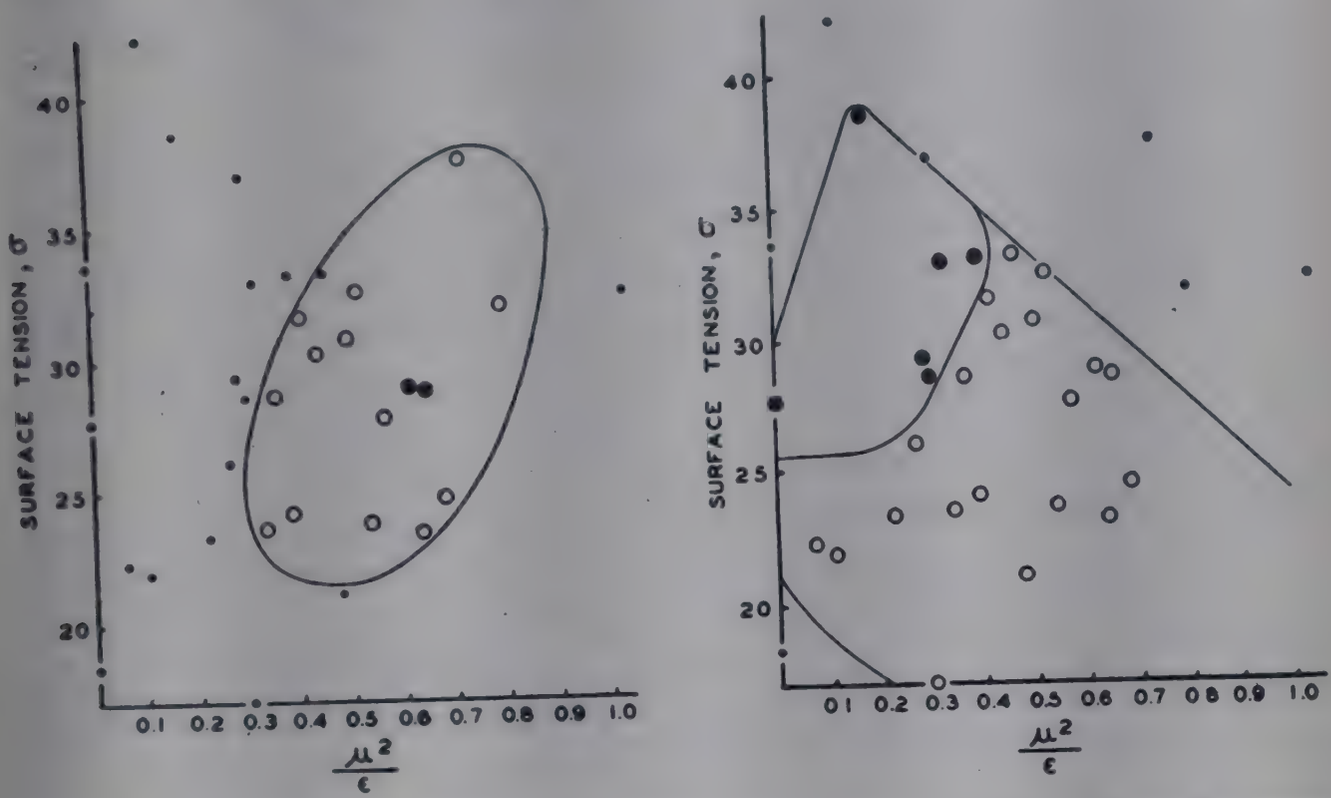

FIG. 2.—CORRELATION OF PHYSICAL PROPERTIES OF CELLULOSE DERIVATIVE SOLVENTS WITH SOLVENT POWER (MOLL[50]).

A—Cellulose trinitrate in aliphatic solvents.
B—Ethylcellulose in aliphatic solvents

μ—Dipole moment.
ϵ—Dielectric constant.
●—Complete solution.
○—Partial solution.
•—Undissolved.

may be sufficient for satisfactory plasticization. In fact, such powerful solvents as acetone leave a considerable attraction between chains which manifests itself by an abnormally high viscosity in high concentrations, unless an alcohol or organic acid is present to solvate the hydroxyl groups.

In the case of cellulose ethers, there is no evidence for solvation of the alkoxyl group. The highly substituted ethers are soluble in aromatic hydrocarbons, ethers, and chlorinated solvents. The essential thing here is to have approximately the same internal pressure in the solvent

[50] W. L. H. Moll, *Kolloid-Beihefte*, **49**, 1 (1939).

and in the derivative.[1] If, however, there is a considerable content of hydroxyl groups in the ether (0.5 or more per C_6), alcohols are of very considerable help in promoting solubility.

The solubility of the less highly substituted ethers is discussed in detail in Section E of Chapter VIII. Here, the essential factor is the introduction of enough bulky substituents to lower the regularity of contact. Water then can solvate the hydroxyls and cause solution because of its similarity in internal pressure to the polar derivative.

In addition to this generalization about polar group content, one other concept, based on physical properties, is fairly useful. Ostwald[51, 52] and Ortloff[51] proposed the use of the value μ^2/ϵ (μ = dipole moment, ϵ = dielectric constant), which is a measure of the "mirror-image force," that is, of the force with which a dipole is attracted by its mirror image. This function was not as successful, however, as a modification due to Moll,[50, 53] who plotted μ^2/ϵ against the surface tension, σ (the use of σ was proposed by Papkov[54]) and found a tendency for the active solvents for a given cellulose derivative to be grouped in a small region of this plot (Fig. 2). It was necessary, however, when using this method, to plot aliphatic and aromatic solvents separately, as the regions of solvent power were different in the two cases. There are a few solvents which do not fit into this correlation, which is not surprising in view of the weakness of its theoretical background as pointed out above.[49]

2. Abnormal Viscosity Effects

(*a*) *Gelation*

It is characteristic of solvent–cellulose-derivative systems that, at high concentrations, they set to gels with finite yield points. The best-known of such systems is "solidified alcohol," which is a solution of several per cent of nitrocellulose to which enough water has been added to cause gelation but not precipitation. Before describing this system, it is well to consider some for which the conditions favoring gelation are better defined.

If a few hundredths of a per cent either of copper powder and any soluble metallic chloride, or of any metal above copper in the electromotive series

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[51] Wo. Ostwald and H. Ortloff, *Kolloid-Z.*, **59**, 25 (1932).
[52] Wo. Ostwald, *J. Oil Colour Chem. Assoc.*, **22**, 31 (1939).
[53] W. L. H. Moll, *Kolloid-Z.*, **85**, 335 (1938).
[54] S. Papkov, *Kolloid-Z.*, **71**, 204 (1935).

and copper chloride is added to a solution of nitrocellulose in an anhydrous solvent, a deep emerald-green firm gel is obtained in a few hours.[55] This gel is immediately broken and the characteristic color lost by the addition of small amounts of water or acids, or by substances, such as fuchsin, which form strong association complexes with copper. The gel formation seems to be due to the formation of a complex between the copper and two reduced nitrate groups, or between cuprous copper and nitrate groups, in adjoining chains. The outstanding fact is that a very small amount of copper is needed to form stable gels, only a few atoms of copper per cellulose chain being sufficient. When it is considered that many of the copper atoms must be so located that they do not contribute to the gel structure, either being on chains each of which has only one copper atom or else being on chains already linked to a network and therefore immobilized, it becomes clear that the gel structure is maintained by rather infrequent cross-links.

If an attempt is made to secure a firmer gel by increasing the amount of copper, it is found that syneresis occurs, the nitrocellulose separating as a distinct, coherent phase. This demonstrates that, if cellulose-derivative solutions are attached to one another along more than a small portion of their length, the only stable state is separation of a cellulose-rich phase, a point of considerable importance in connection with the discussion of micelle formation earlier in this chapter. It must be remembered that these gels are not held by primary valence cross-links, but rather by forces more intense than, but of the same nature as, the hydrogen bond cross-links assumed as the cause of micelle formation by the proponents thereof. The inherent weakness of these bonds is indicated by the thixotropic behavior of relatively thin copper gels, which may be converted to thin liquids by rapid stirring, but set up to gels again on standing.

Another system equally easy to interpret is furnished by cellulose derivatives, such as ethylcellulose or cellulose acetate, in which a few acid groups have been introduced either by oxidation, by formation of the half-ester of sulfuric or a dibasic organic acid, or by reaction with sodium chloroacetate in the presence of alkali. If these acid groups are neutralized by sodium, and the derivative is dissolved in a nonpolar solvent, such as benzene or a chlorinated solvent, a gel is obtained. These gels are easily broken by addition of alcohol, and they are broken by shaking but form again on standing. As in the previous case, the gel formation must be due to relatively weak points of attachment at a few places along the chain, this time due to dipole interaction. Again, as in the previous case, if

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[55] W. E. Gloor and H. M. Spurlin, *J. Am. Chem. Soc.*, **58**, 854 (1936).

too many such groups are present, the derivative becomes insoluble i nonpolar solvents.

These facts are of great value in clarifying the theory of thixot ropy. It is clear that the mechanism in these cases is that, on rapi stirring, the active points of attachment are broken loose from one anothe and are mixed up in the solution. On standing, diffusion causes the group to come close to one another, with resultant immobilization of the ad joining portions of the two chains. If the chains have all become immo bilized, further diffusion is hindered, and other active groups do not hav a chance to become involved in cross-linkage. No action-at-a-distance o other complicated phenomena need to be called into play; it is likely that this will also be found to be the case in all other cases of thixotropy.

In the case of the water-alcohol-nitrocellulose gels mentioned above, there are many potential points of attachment along the chain, due to adhesion of unsolvated portions of the molecule. It is therefore understandable that these gels require a very delicate balance of solvent power for reasonable stability. Even then, they tend to liquefy on cooling, due to increased solvation, and to synerize on standing or stirring. The syneresis on stirring, which is opposite in behavior to the gels with only a few potential points of attachment between chains, is an indication that, if many points of attachment are available and if the immobilization due to gelation discussed above is disturbed, some chains will be brought into position such that they may adhere along considerable portions of their length, with resultant insolubilization.

The tendency for gel formation increases rapidly with concentration and with molecular weight. If the concentration is high, there is a better chance that enough of those chains having two or more potential gel points per chain are present to form a three-dimensional network throughout the system; in addition, the mass action effect promotes linkage in the case of gelation by means of relatively weak linkages. If the molecules are longer, there is a greater chance that there will be two or more gel points per chain.

From the properties of cellulose-derivative gels, it is easy to see that many molecules do not take part in gel formation. It is frequently possible to leach these out by use of a solvent which does not disperse the gel structure. The miscibility of these individual molecules with the gel structure emphasizes the fact that most of the length of the molecules involved in the gel structure is unaltered and can move about freely, without excessive stretching of the molecules, in the restricted part of the solution available.

The close analogy between the gels discussed here and the swollen condition described for fibers in Chapter III and Chapter VIII, D is apparent. In the latter case, a limit is placed on the tendency of the amorphous material to dissolve by its attachment to morphological elements of structure, or by its enclosure in a pocket from which it cannot escape. In the case of typical gels, the immobilizing network is distributed at random throughout the system rather than being a well-defined separate phase, as is the case with fibers.

(*b*) *Viscosity-Concentration Relationships*

The firm gels mentioned above are, of course, only an extreme case of a type of phenomenon which occurs to some extent in any solution of a cellulose derivative containing portions of the chain free of substituent,

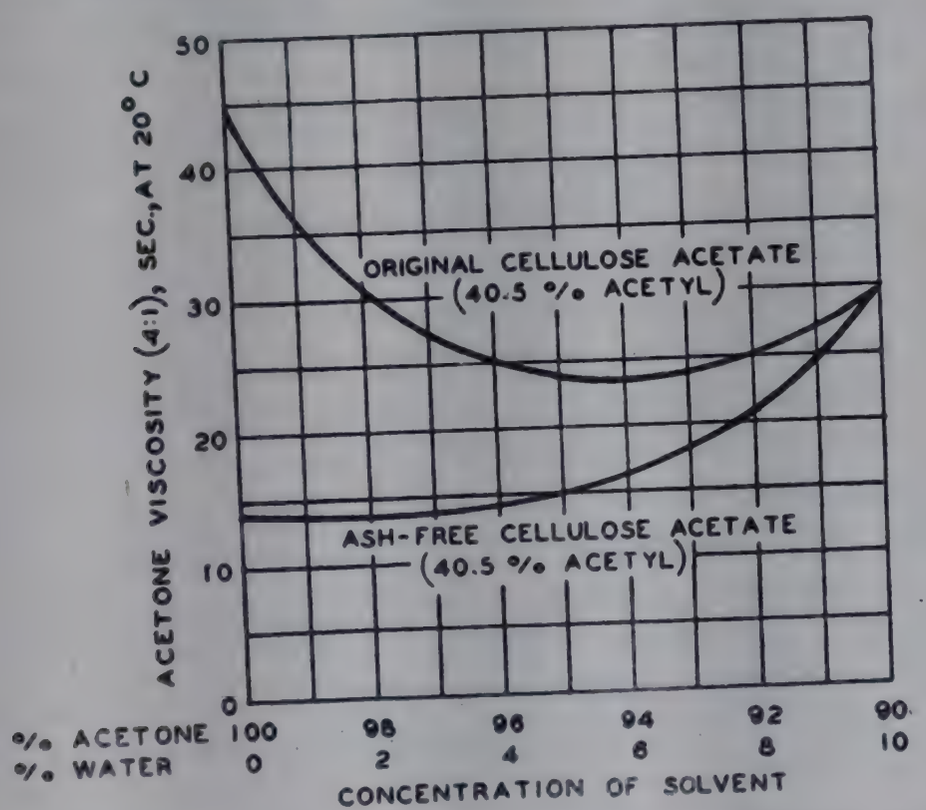

FIG. 3.—EFFECT OF BOUND ASH AND WATER CONTENT ON VISCOSITY OF CELLULOSE ACETATE IN ACETONE (MALM[55a]).

carboxyl groups neutralized with metal ions, or any other factor promoting gelation. As has been pointed out by Flory,[56] if the functionality and the degree of reaction of the functional groups (in this case, the number of

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[55a] C. J. Malm (to Eastman Kodak Co.), U. S. Patents 2,126,488–9 (May 7, 1936).

[56] P. J. Flory, *J. Am. Chem. Soc.*, 63, 3083, 3091, 3096 (1941).

gelation points per cellulose chain) is less than a certain amount, a three-dimensional network will not exist throughout the mass of material, although there will be many cases of two or more molecules being held together. These aggregates must not be visualized as micelles, but rather as branched molecules. The greater the amount of such aggregation, the higher will be the viscosity of the solution. Micelle formation, on the contrary, would tend to reduce viscosity.

As was pointed out previously, the typical cellulose derivatives all exhibit about the same type of viscosity-concentration relationships. If, however, there is much possibility of association of ion pairs, or of any other type of joining such as is responsible for gelation, this phenomenon will be greatly promoted by an increase of concentration, as was pointed out under the topic of gelation. There has been a considerable amount of work on the influence of various metallic ions, present either as bound ash or as added metallic salt, on the viscosity-concentration relationships of commercial cellulose derivatives.[55a, 57–64]

The magnitude of the observed effect in 20% solution may be grasped readily from Figure 3, originally published by Malm.[55a] This figure brings out the further fact that addition of water nullifies the effect of the metallic ion. As was pointed out by Lohmann,[64] alcohols have the same action. In the work cited, however, it does not appear that the two different effects have been adequately separated. The theoretical interpretations advanced have been based on the observation that calcium chloride will markedly enhance the viscosity of cellulose acetate, the effect being roughly proportional to the content of hydroxyl groups. This effect is undoubtedly due to the formation of a complex with the hydroxyl ions of the cellulose derivative, quite analogous to the complex formed between calcium chloride and alcohol. This complex will have the same tendency to associate with similar complexes in adjoining chains as is displayed by ion pairs. There is the further possibility that the calcium chloride will

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[57] A. V. Pamfilov and M. G. Shikher, *Colloid J.* (*U.S.S.R.*), **4**, 587 (1938).

[58] Z. Rogovin and coworkers, *Org. Chem. Ind.* (*U.S.S.R.*), **1**, 285 (1936); **3**, 274 (1937); **4**, 425 (1937).

[59] Z. Rogovin and M. Ioffe, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 2167 (1937).

[60] Z. Rogovin and M. Ioffe, *J. Applied Chem.* (*U.S.S.R.*), **12**, 269 (1939).

[61] S. A. Glikman, *J. Gen. Chem.* (*U.S.S.R.*), **11**, 512, 678 (1938).

[62] L. T. Vodyakov, *Trans. Kirov Inst. Chem. Tech. Kazan*, **8**, 61 (1940).

[63] S. Papkov, *J. Phys. Chem.* (*U.S.S.R.*), **10**, 418 (1937).

[64] H. Lohmann, *J. prakt. Chem.*, **155**, 299 (1940).

enter into complex formation with hydroxyls of adjoining chains, thus linking them together.

It must not be forgotten, however, that it has been adequately demonstrated (Chapter II, H) that the metal content of cellulose itself, not readily removed by washing and therefore still present in commercial derivatives, is largely bound to acid groups in the cellulose or in an impurity such as pectin admixed therewith. That the same is true for nitrocellulose was shown by Landon.[66] In this case, the combined sulfuric acid, present as half-ester, holds metallic ions very tenaciously. Many of the samples of cellulose acetate which have been described in the literature as possessing abnormal viscosity-concentration curves undoubtedly contained appreciable amounts of combined sulfuric acid. The ash, especially divalent cations such as calcium, bound to acid groups undoubtedly plays a large role in causing the abnormally high viscosities at high concentrations in nonaqueous hydroxyl-free solvents. It is unlikely that the sample of cellulose acetate from which the data of Figure 3 were taken contained sufficient free metallic salt to form enough complexes of the type observed with calcium chloride to cause the observed effects.

The effect of water and of alcohols in breaking the association leading to high viscosity in the case of bound ash may be ascribed to two factors: first, solvation of the calcium ion, which will increase its bulk and prevent close contact of ion pairs, as well as lower its tendency to solvate with the hydroxyls of an adjoining chain; and, second, increase of the dielectric constant of the solvent, which will force the calcium ion farther, on the average, from the cellulose chain and permit greater mobility of the chains with respect to the calcium ion.

In addition to the abnormal viscosity due to metallic ion content, two other factors must be considered. One of these, a tendency toward association due to poor solvent power, is discussed below, under determination of solvent power by viscosity measurements. The other is due to the presence of essentially insoluble impurities. Nonuniform products, especially those containing remnants of fiber structure, are especially prone to this type of behavior.

It is characteristic of all of the types of abnormal viscosity behavior discussed here that, in extremely dilute solutions, even in the absence of hydroxyl-containing solvents, the association disappears and correct molecular weights are obtained by the Staudinger viscosity method.[64] This fact demonstrates the relative weakness of the association forces.

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[66] M. Landon, *Mém. poudres*, **27**, 190 (1937).

3. Determination of Solvent Power

(a) *Relation between Solvent Power and Viscosity*

The most generally accepted measure of solvent power is the viscosity of concentrated solutions (10–25% by weight) of cellulose derivatives.[67] This, of course, does not agree at all with theoretical concepts such as those advanced previously in this chapter and further discussed in Sections B and E. According to these considerations, the viscosity of a perfect dispersion of a long-chain molecule will be determined by the viscosity of the solvent, the average length and width of the solvated chain, and any influence solvation has on internal mobility of the chain. In order to present the reasons for the actual usefulness of viscosity as a measure of solvent power, this subject is treated after gelation and abnormal viscosity.

The commercially useful solvents are of relatively low viscosity and do not differ greatly among themselves in viscosity. Therefore, the effect of solvent viscosity is almost a constant factor in these comparisons. Then, too, the degree of substitution of the commercially important derivatives, nitrocellulose, cellulose acetate, and ethylcellulose, is usually in the range 2.2–2.6. The fairly high hydroxyl content of these substances leaves ample opportunity for hydrogen bonding between chains if the average distance between chains is small because of low solvation of the chain as a whole, or if the hydroxyl groups are not themselves tied up by solvate formation. In high concentrations of cellulose derivatives in mixed solvents, there may be an actual shortage of active solvent molecules. Thus, in the case of a weakly solvating solvent or a solvent mixed with much inert diluent, there will be ample opportunity for occasional weak linkages of the type postulated above for gelation. Even an average of two such linkages per chain occurring at one time would result in an enormous increase in viscosity. It is evident, then, that, as long as comparisons are confined to solvents of approximately the same viscosity, the measurement of viscosity of concentrated solutions will be some measure of solvating power.

Comparisons between the solvent power of viscous liquids, such as commercial plasticizers, and low-molecular-weight solvents are clearly invalid. In this case, comparisons based on relative viscosity or on specific viscosity would possess much more merit. It would indeed be welcome if such comparisons were always made on the basis of relative viscosity. However, it must be remembered that the average width of the solvated

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[67] O. Jordan, *Technology of Solvents*. Hill, London, 1937.

chain may be much greater in the case of high-molecular-weight solvents such as plasticizers, and the relative viscosity may be correspondingly high, even though the material may be a perfectly good solvent. Also, with solvents of high molecular weight, a weight of solvent much greater than that of the cellulose derivative may be tied up by solvation, so that a 10% solution based on dry weight may actually be a 20% or even 30% solution of the solvated derivative.

(*b*) *Dilution Ratio*

Another widely used measure of solvent power is furnished by the determination of the amount of some nonsolvent that must be added to a solution before initial precipitation occurs. This method is theoretically much sounder than the one based on viscosity measurements, and is displacing it to an increasing extent. The basis of the dilution ratio method is, of course, that increasing dilution increases the tendency for the solvating molecules to leave the cellulose chain and therefore increases the attractive forces between chains. A quantitative evaluation of the results presupposes a determination of the activity of the solvent at the concentration where precipitation occurs. This is never attempted in practice, but fortunately most commercial solvents do not depart very far from ideality in solution in toluene, the commonly used diluent. This is not, of course, true for alcohols and other very polar solvents.

The great weakness of the dilution ratio method lies in the fact that the first portions of diluent may actually greatly improve the solvent power of the medium. This is especially true of very polar solvents such as alcohol. In these cases, the effect is due to the fact that the solvated cellulose derivative has a lower internal pressure than the solvent, and, as was discussed under ether-alcohol mixtures, the diluent serves to lower the internal pressure of the solvent without affecting the composition of the solvated cellulose chain. Also, the tendency to desolvate the chain is lessened by the great difference in internal pressure of the solvent and the diluent, which causes the activity of the solvent to remain quite high even after much diluent has been added. Because of these effects, the dilution ratio method is useless for solvents containing large quantities of alcohols or organic acids if a true measure of solvent power is desired. The dilution ratio determination has, even in the case of alcohols, a great practical value in the economic evaluation of solvents, as it is a measure of the extent to which the more expensive polar solvents may be partially replaced by inexpensive diluents.

4. Separation into Two Phases

(a) *Fractionation into Components of High and Low Molecular Weight*

It has long been known that cellulose derivatives are not homogeneous; fractional extraction or fractional solution makes possible a separation into fractions of differing properties. It was shown by Duclaux and Wollman[68] that these fractions are different in molecular weight and in viscosity but do not differ in composition. Since then there have been many investigations of this kind, both in an effort to enlarge the theory of cellulose structure and in the endeavor to discover methods of improving the

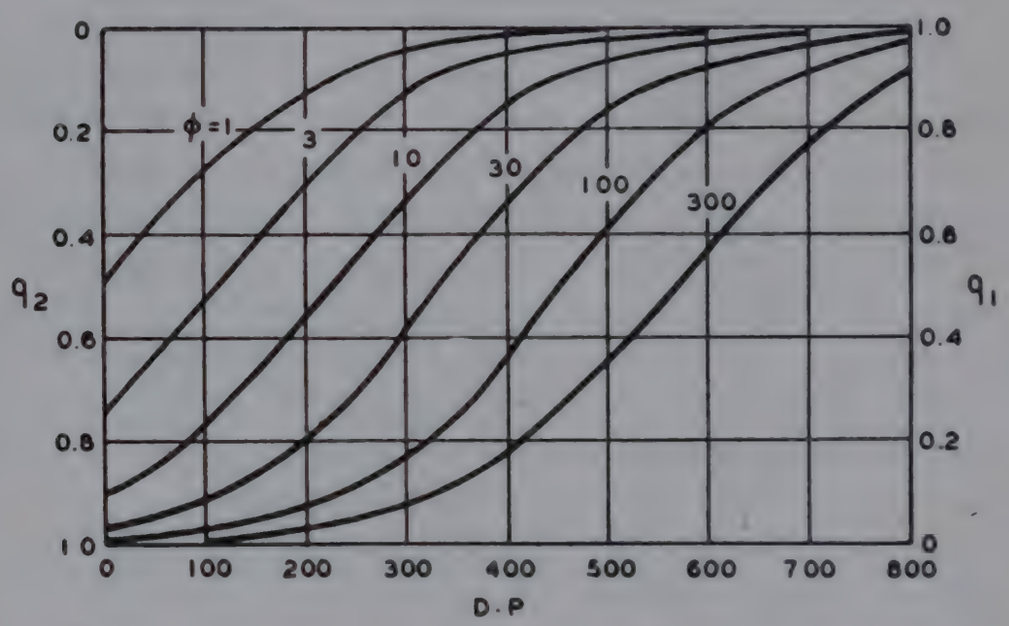

FIG. 4.—DEPENDENCE OF DISTRIBUTION OF POLYMER FRACTIONS BETWEEN TWO PHASES, AS A FUNCTION OF THE VOLUMES OF THE PHASES (SCHULZ AND NORDT[69]).

Energy difference per monomer unit (E_0) between phases assumed to be 6 cal.
Temperature = 300°A.
q_1 = Grams of material of a given D.P. in phase 1 (precipitate phase).
q_2 = Grams of material of a given D.P. in phase 2 (supernatant phase).
$\phi = \frac{V_2}{V_1}$ = Ratio of volumes of phases 2 and 1.

physical properties of cellulose derivatives. The latter subject is treated in Section D of this chapter.

As was indicated above, and is demonstrated more rigorously in Section B

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[68] J. Duclaux and E. Wollman, *Bull. soc. chim.*, [4], **27**, 414 (1920).
[69] G. V. Schulz and E. Nordt, *J. prakt. Chem.*, **155**, 115 (1940).

of this chapter, the solubility of long-chain molecules in a solvent in which they are only slightly soluble is an exponential function of the length of the chain, the longer chains being the more insoluble. Using the concept that the attraction between chains is proportional to their length, but neglecting the entropy of dilution considered in Section B, Schulz[69, 70] has calculated the degree of fractionation for various conditions of fractional precipitation. As is shown in Section B, his result is in the same general form as the theoretically exact one, and may be used with confidence.

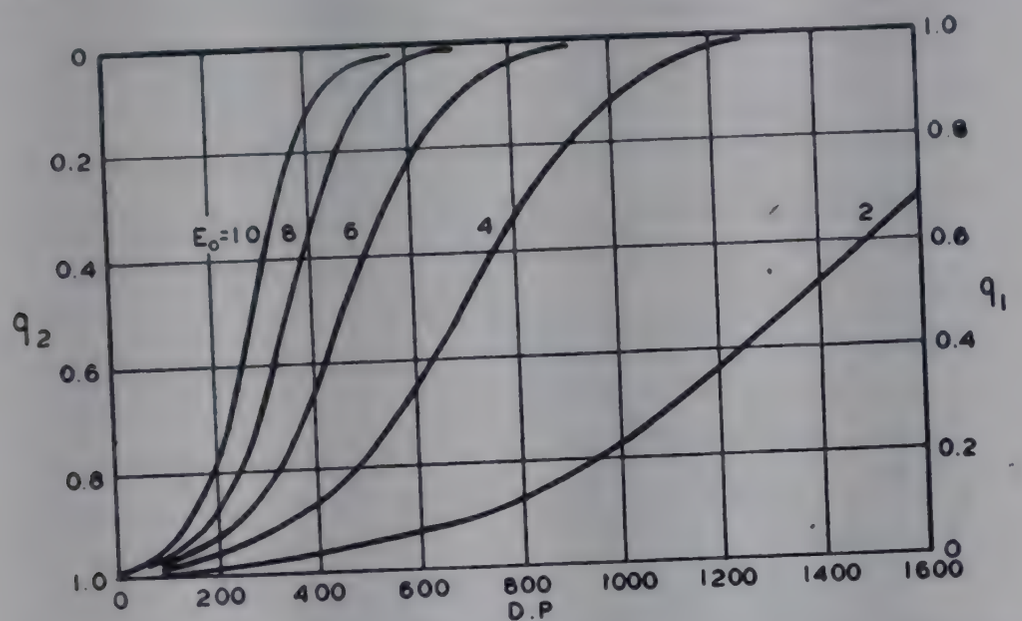

FIG. 5.—DEPENDENCE OF DISTRIBUTION OF POLYMER FRACTIONS BETWEEN TWO PHASES, AS A FUNCTION OF THE ENERGY DIFFERENCE BETWEEN THE PHASES (SCHULZ AND NORDT[69]).

Ratio of volumes of phases = 100.
Temperature = 300°A.
q_1 = Grams of material of a given D.P. in phase 1 (precipitate phase).
q_2 = Grams of material of a given D.P. in phase 2 (supernatant phase).
E_0 = Energy difference per monomer unit between phases.

Schulz started with the observation that, if the solvent is powerful enough to dissolve all the smaller chains, the remainder is usually present as a highly swollen mass which shows all the usual properties of a liquid phase. He made the additional observation that, when conditions are such that the undissolved material is so concentrated that its viscosity does not allow quick attainment of equilibrium, or when the solid phase is crystalline (the latter condition is never observed during the precipitation of cellulose products but is encountered with some condensation polymers), fractionation is very difficult. Therefore, for the cases where fractionation is the objective,

[70] G. V. Schulz, *Z. physik. Chem.*, **B46**, 137 (1940).

the process may be treated as one of distribution of a solute between two immiscible liquids.

The mathematical treatment of Schulz is out of place here, but the results are of interest (Figs. 4, 5, and 6).

Figure 4 shows that, as the size of the polymer increases, other conditions being constant, an increasing volume of the supernatant phase is necessary in order to get that polymer into solution.

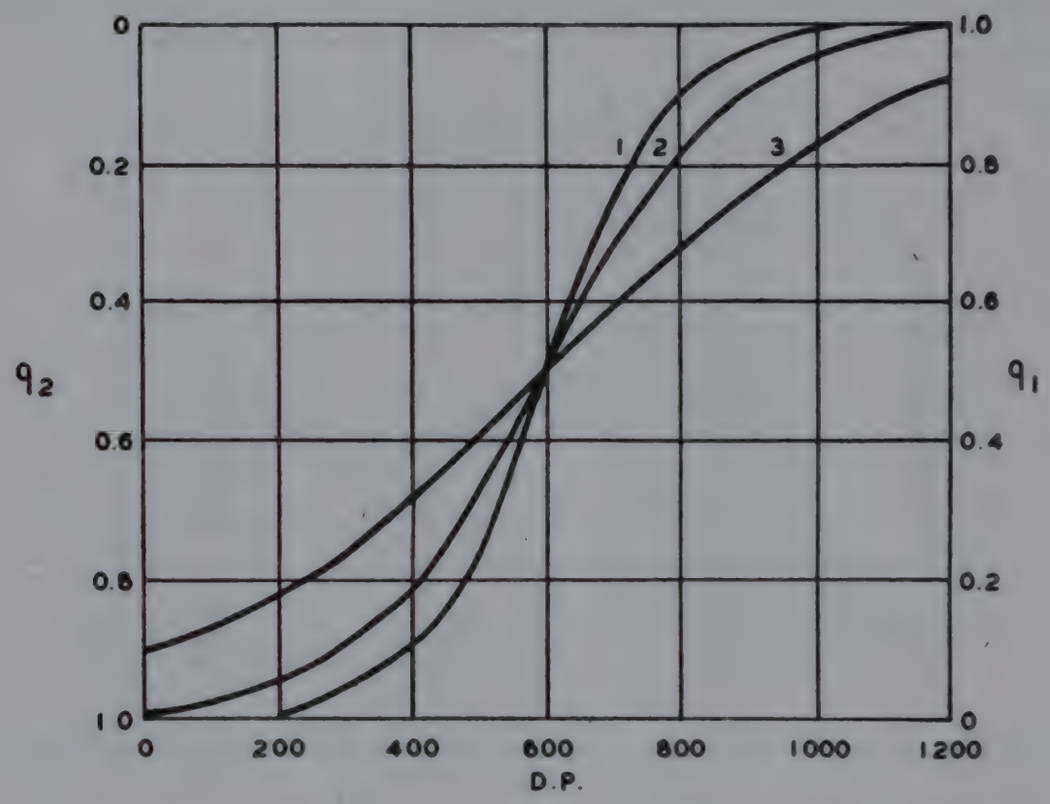

FIG. 6.—DEPENDENCE OF DISTRIBUTION OF POLYMER FRACTIONS ON PHASE VOLUMES AND ON ENERGY DIFFERENCES WHEN ONE-HALF OF MATERIAL OF D.P. 600 IS IN EACH PHASE (SCHULZ AND NORDT[89]).

Curve 1: $\phi = 1000$; $E_0 = 6.9$ cal.
Curve 2: $\phi = 100$; $E_0 = 4.6$ cal.
Curve 3: $\phi = 10$; $E_0 = 2.3$ cal.
q_1 = Grams of material of a given D.P. in phase 1 (precipitate phase).
q_2 = Grams of material of a given D.P. in phase 2 (supernatant phase).
$\phi = \frac{V_2}{V_1}$ = Ratio of volumes of phases 2 and 1.
E_0 = Energy difference per monomer unit between phases.

It is, of course, possible to vary the energy difference, E_0, per monomer unit between the two phases, by varying the amount of diluent. Figure 5 shows that for a given ratio of volumes, an increase in E_0 (an increase in diluent) tends to throw the polymer into the precipitate phase. It is thus obvious that both the ratio of volumes and the amount of diluent may be

ıdependently adjusted in order to get a desired proportion of polymer f given D.P. into solution. Therefore, it is necessary to compare the eparation curves for different combinations of E_0 and ϕ so chosen that naterial of a given degree of polymerization has a constant separation ratio. This is done in Figure 6, choosing conditions such that half of the polymer of D.P. = 600 is in each phase. It is immediately apparent that the separation is much sharper for high volume ratios and high values of E_0 (that is high concentration of diluent).

In practical terms this means that precipitation is the more effective, the smaller the amount of material in the precipitate. This can only be the case if a large number of fractions are taken, a factor frequently overlooked in practice. Thus, if only a small number of final fractions is desired, it is better to add the diluent in small increments, separate the precipitate after each addition, and then combine fractions of desired properties, rather than to take one big fraction in this range.

Another factor to be considered is that if a given proportion of the material is precipitated from a concentrated solution, the volume of the precipitate phase will be a greater fraction of the total volume than if the solution were dilute. This is a consequence of the fact that the activity of the solvent in concentrated solutions is independent of chain length. Therefore, in concentrated solutions, a much greater number of fractions must be collected in order to achieve the same degree of fractionation that a smaller number from a more dilute solution would give.

Three further conclusions can be drawn from Schulz's work.[70] First, under ordinary conditions of fractionation, the shape of the distribution curve may be determined with about as much accuracy after refractionating the fractions once as is possible after many more fractionations. Second, the ease of obtaining fractions of the same percentage uniformity is about the same for large polymers as for small. Finally, there is not much hope for securing fractions sharper than $\pm$ 5% variation from the mean by repeated fractionation. Experimental data bearing out the first of these conclusions may be found in the recent article of Sookne, Rutherford, Mark, and Harris.[24] The second conclusion is probably not quite accurate, as more exact calculations tend to show that, for comparable conditions of fractionation, separation becomes more difficult as molecular weight increases. As for the third conclusion, certainly no one has even claimed this degree of fractionation up to now.

As the mathematical treatment of Schulz[70] is based on the assumption that solubility decreases exponentially as the chain length increases, which

is a consequence of almost any theory of solubility (see Section B of this chapter), it may be assumed that his conclusions are very generally applicable. Certainly they are not inconsistent with observation. The requirement that fractionation must be carried out in dilute solution to be effective is generally recognized. It is unfortunately true that too often the requirement that a large number of fractions must be taken has been neglected. However, fractionation as usually carried out is proving to be an effective tool for research on cellulose derivatives, as is shown by the continuing stream of papers on this subject.

(*b*) *Activity of Solvents in Solutions*

The general treatment of this subject is given in Section B of this chapter. The present discussion is limited to a review of some of the available data, together with suggestions for further developments.

One factor, which can be treated logically after the discussion of fractionation, is the very characteristic behavior of the activity of a solvent with a change in its solvent power for a given derivative. The experimental development of this subject is largely due to Dobry,[71] who has measured the osmotic pressure of a number of systems whose solvent power was varied up to and beyond the point where separation into two phases occurs. The data in Figure 7A and Figure 7B for cellulose acetate in chloroform-alchohol mixtures are typical. It will be observed that, as the solvent power of the medium is lowered by lowering the alcohol content, the slope of the curves of osmotic pressure/concentration (P/C) versus concentration (C) is decreased. When the curve is horizontal, further lowering of the alcohol content causes a separation into two phases. It is thus apparent that the lowering of the activity of the solvent (the lowering is more pronounced, the steeper the curve) is a measure of solvent power; Dobry[71] appears justified in her contention that this is the best measure of solvent power available.

On separation of the system into two phases, the supernatant liquor contains lower-molecular-weight material than the precipitate. In Figure 7B is plotted the variation of P/C for the supernatant phases with further dilution with solvent of the same concentration. These upper layers are, of course, on the point of precipitation. The curves show that for materials of different molecular weight, the P/C curves are horizontal for that solvent composition which barely suffices for solution.

A consequence of these results which is of importance for the theory

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[71] A. Dobry, *J. chim. phys.*, **36**, 102 (1939).

of fractionation is that, at least up to fairly high concentrations under conditions where two phases coexist (if the solvent has the same composition in both phases, as it does in the case of chloroform-alcohol with cellulose acetate, or if a pure compound is used as solvent and fractionation is secured by varying the temperature), the activity of the solute molecules in the supernatant phase is that demanded by Raoult's law. It seems hardly possible that this is due to a compensation effect, such as would occur if the larger molecules had an activity greater than that demanded by Raoult's law, and if the smaller molecules had a correspondingly lower activity. Therefore, it is justifiable to calculate the distribution functions

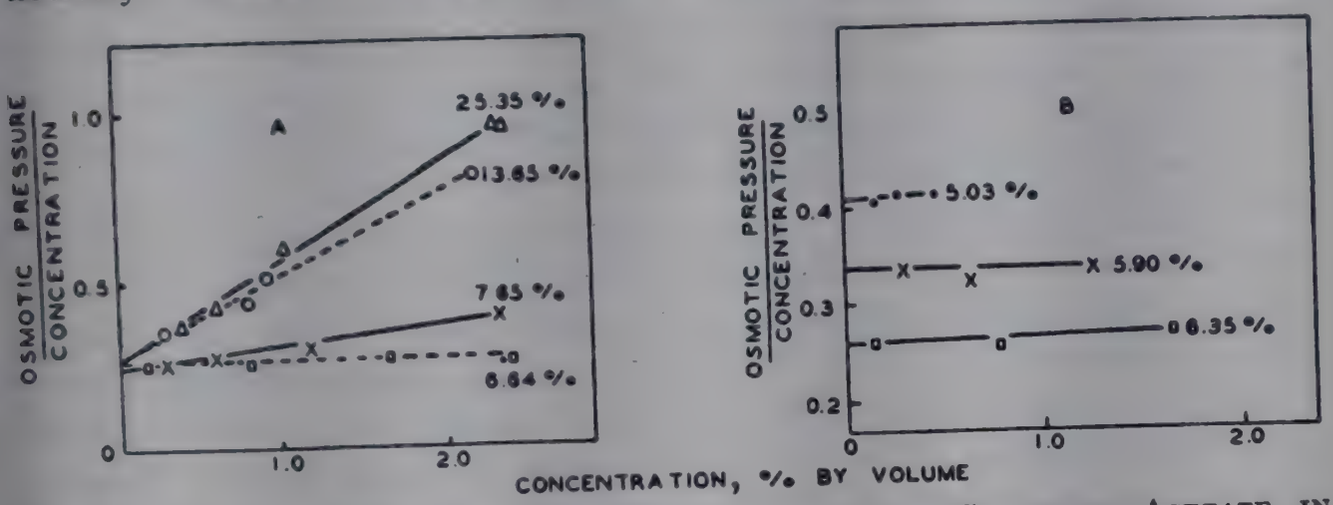

FIG. 7.—OSMOTIC PRESSURE-CONCENTRATION CURVES FOR CELLULOSE ACETATE IN CHLOROFORM–ALCOHOL MIXTURES (DOBRY[71]).

A—One sample of acetate in different solvent mixtures.
B—Samples of three fractions of the above acetate in solvents of such concentration that the solutions are at the point of precipitation.

of the individual kinds of solute molecules between the two phases on the basis of ideal solutions in the more dilute phase. Whether this is true for the more concentrated phase remains to be demonstrated, but it appears likely to be so in view of the theoretical conclusions in Section B, especially in cases where the bottom phase is of relatively low concentration (3–7% in Dobry's[71] work).

(c) *Miscibility of Derivatives in Solution*

An interesting problem is presented in the behavior of mixtures of cellulose derivatives in solution in a solvent which will dissolve either alone. A few cases are known where derivatives are miscible in all proportions, for instance, ethylcellulose and nitrocellulose. In most cases, if a mixture of derivatives is examined in gradually increasing concentration, a point is reached where a separation into two phases is observed. The relative

concentration of the two phases varies greatly from case to case. Much could be learned about the interaction between solute molecules in solution and their relative affinity for solvent by a systematic study of such systems. This does not appear to have been attempted as yet.

5. Aging Effects in Solutions

A good deal of confusion has arisen in the past due to attempts to explain changes of properties of solutions on standing by analogy with aging of inorganic colloids, such as silica gel and ferric oxide sol. Such effects are due to changes in the degree of specific interaction between the dispersed particles and are frequently a sign of lack of equilibrium in the solution. While these effects are often present in cellulose solutions, they are not so important as degradation and change in degree of substitution.

A complete treatment of this subject, together with a bibliography, has been given by Wehr.[72] Some important observations which Wehr made in the case of nitrocellulose are worth discussion in this brief treatment. High-viscosity types degrade more rapidly than low-viscosity types, but the curves never cross. The changes are irreversible, precipitation and resolution giving the viscosity of the degraded solution, not the starting viscosity. At higher temperatures, the reduction in viscosity continues indefinitely, though, at room temperature, the degradation appears to cease after a time. The rate of degradation in a given solvent is independent of concentration. All of these factors are explained on the assumption that the drop in viscosity is due to a shortening of the average chain length. The chance of a chain break occurring is, of course, greater as the chain becomes longer, and the effect of a given reduction in molecular weight on viscosity is much greater if the original chain is very long. A kinetic study of the process showed that the rate of breaking of bonds was the same in all viscosity ranges of nitrocellulose, exactly as was found by Freudenberg[16] and Ekenstam[12] in the case of the degradation of cellulose by acids.

Oxygen is not a factor in nitrocellulose degradation[72] (unpublished experiments by the writer have led to the same conclusion). However, organic peroxides hasten degradation, and the usual oxidation and polymerization inhibitors of neutral type, such as hydroquinone, slow down the degradation. Acids and bases accelerate degradation, as is shown in the accompanying hitherto unpublished curves (Figs. 8, 9, and 10). A further unpublished observation is that a series of solvents may be set up of gradually

[72] W. Wehr, *Kolloid-Z.*, **88**, 185, 290 (1939).

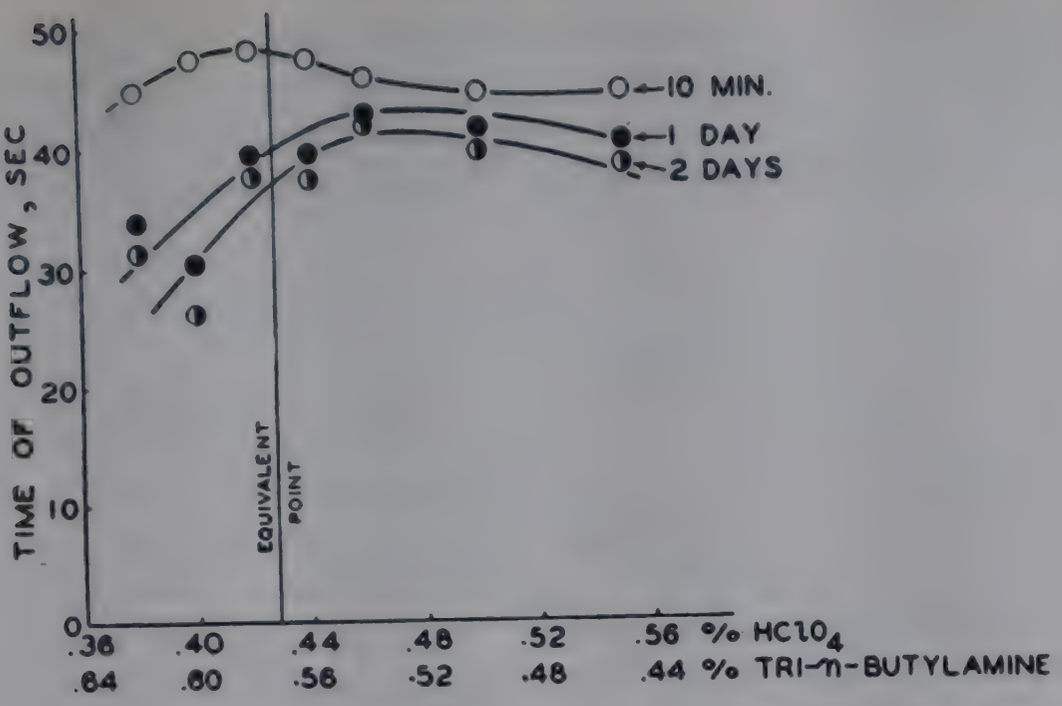

FIG. 8.—DEGRADATION OF NITROCELLULOSE IN PRESENCE OF ACID AND BASE DURING STORAGE AT 25°C.

Ten per cent by weight of 1/2-sec. "RS" nitrocellulose in butyl acetate containing 1% total $HClO_4$ and tri-*n*-butylamine.

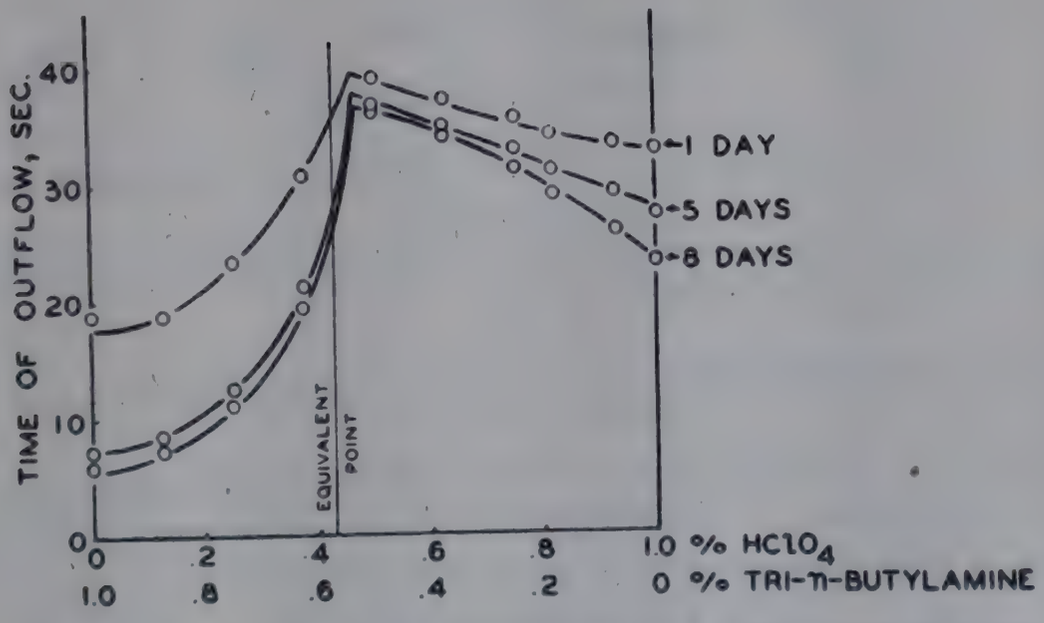

FIG. 9.—DEGRADATION OF NITROCELLULOSE IN PRESENCE OF ACID AND BASE DURING STORAGE AT 25°C.

Ten per cent by weight of 1/2-sec. "RS" nitrocellulose in butyl acetate containing 1% total $HClO_4$ and tri-*n*-butylamine.

increasing tendency to degrade nitrocellulose, in order: 40% butyl acetate, 60% toluene, pure butyl acetate, ethyl acetoacetate, butyl lactate, Cellosolve acetate, Cellosolve, and cyclohexanone. Organic bases lead to an even more rapid degradation. Wehr[72] seems not to have observed this

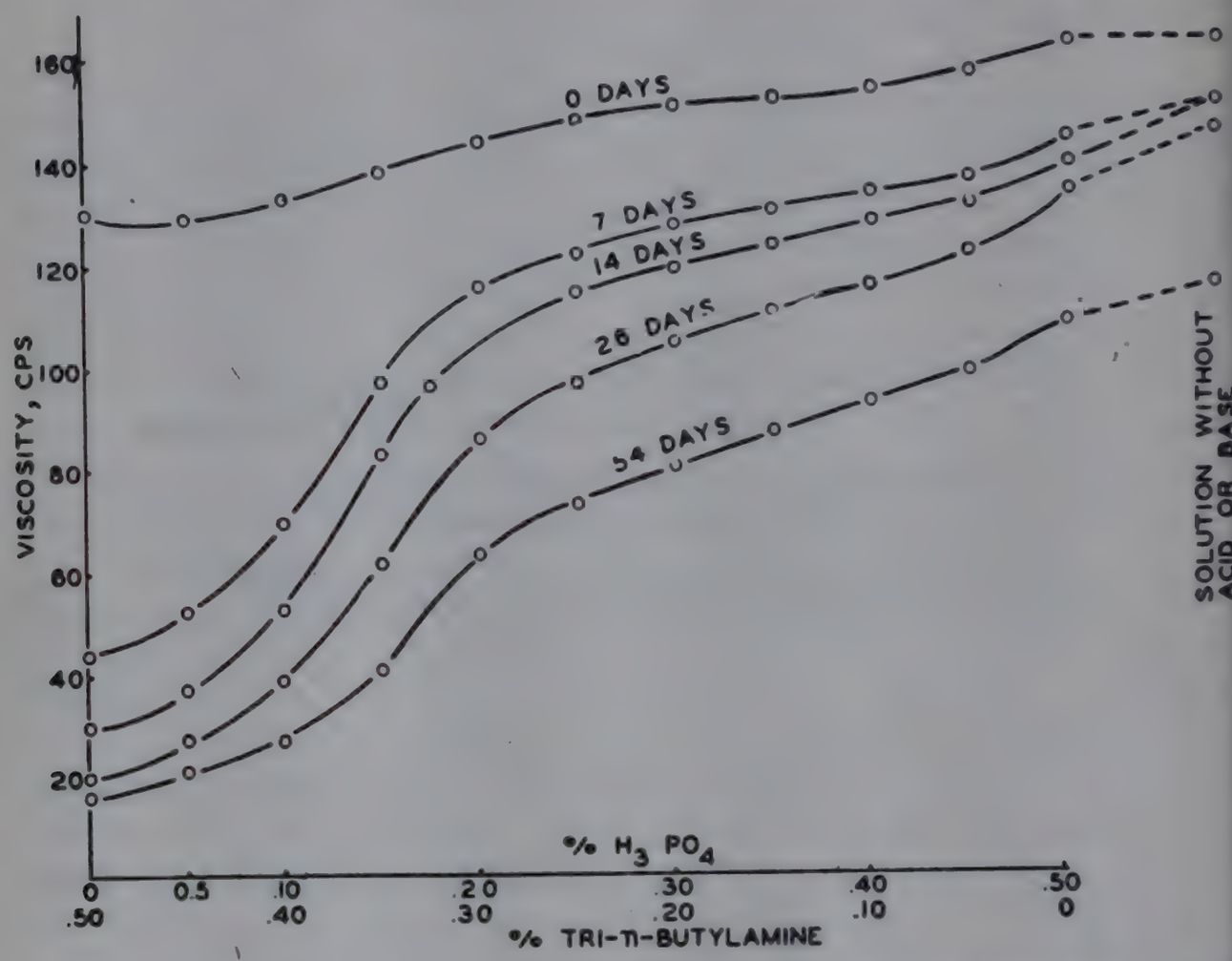

FIG. 10.—DEGRADATION OF NITROCELLULOSE IN PRESENCE OF ACID AND BASE DURING STORAGE AT 25°C.

Ten per cent by weight of 1/2-sec. "RS" nitrocellulose in Cellosolve containing 0.5% total $HClO_4$ and tri-*n*-butylamine.

relationship because he tested only two solvents, butyl acetate and methyl ethyl ketone.

As a result of these observations, it appears very likely that the degradation of nitrocellulose is a chain reaction catalyzed by bases, and that the variation of activity of solvents in causing degradation is due to a variation in their basicity. In this connection it is interesting to note that Lucas and Hammett[73] have shown that the base-catalyzed decomposition of benzyl nitrate is slowed and is completely changed in character by in-

[73] G. R. Lucas and L. P. Hammett, *J. Am. Chem. Soc.*, 64, 1928 (1942).

hibitors. Another pertinent point is that the gas evolved on heating nitrocellulose solutions containing weak bases is largely NO,[74] and the reaction is slowed but not completely inhibited by addition of acids. This is also evident from Figures 8, 9, and 10, where it is seen that the point of minimum degradation is on the acid side. The base- and solvent-catalyzed degradations of nitrocellulose in solution thus appear to be internal oxidation-reduction reactions involving scission of the chain. The well-known degradation of cellulose on denitration with polysulfides is an example of this type of reaction.

Esters of cellulose with organic acids are very stable in solution. Oxygen accelerates their degradation slightly, but organic acids have no effect. Strong mineral acids cause degradation of cellulose acetate, although the reaction is slower than with cellulose itself. Cellulose organic ester solutions, because of their stability, are very suitable for experimental work on the theory of solutions.

Cellulose ether solutions are quite sensitive to oxygen,[72] especially under the influence of light. This action may be practically eliminated by addition of oxidation inhibitors. Benzylcellulose is much more sensitive to oxygen than is ethylcellulose. All cellulose ethers are quite stable to alkalies in the absence of oxygen.

Films prepared from cellulose-derivative solutions have the same properties, regardless of whether an originally low-viscosity type was used or whether a solution of a high-viscosity type was degraded to the same viscosity. This is further evidence that the viscosity lowering is caused by degradation and is not a typical colloidal effect.

The characteristic lowering of viscosity of cellulose derivatives in solution is evidently due almost always to chain breaking. An exception, of course, is the rapid change which occurs immediately after dissolving before equilibrium has been reached. The changes of state characteristic of lyophobic colloids, if they occur with cellulose derivatives, are always associated with abnormally high viscosities, and frequently are associated with slow changes due to the difficulty of establishing equilibrium. Such effects were treated previously under the topic "Gelation." Some other phenomena should be noted for the sake of completeness. If cellulose solutions contain suspended matter, changes in viscosity due to settling or flocculation may be anticipated. One frequently overlooked source of such suspended matter is the irreversible change that often occurs on the surface of precipitated or dried products. For example, if a solution of nitrocellulose

[74] *Prevention of Gas in Pigmented Nitrocellulose Lacquers.* Hercules Powder Co., Wilmington, Del., 1933.

in acetone is precipitated by pouring into water, and if the precipitate is dried and then redissolved, a white haze is observed. This is not encountered if a hydrocarbon is used for precipitation. Another occasional source of changes in viscosity is encountered if an attempt is made to work under conditions where the solvent power is low enough to allow existence of two phases. In some cases, the two phases remain intermixed as an emulsion. The viscosity of such a system depends greatly on the time of standing and on the temperature, a rise in temperature sometimes resulting in an increase of viscosity due to solution of more of the derivative in the continuous phase.

6. Solutions of Cellulose in Aqueous Acids, Bases, and Salts

The insolubility of cellulose in water has excited comment since the beginning of the study of cellulose chemistry. As has been pointed out, this must be due to the fact that cellulose chains fit so well against one another that complete linking of adjoining chains by hydrogen bonding occurs, and to the further fact that the cellulose molecule is rigid enough to prevent a relatively short segment from lifting off without disturbing the neighboring portion of the chain. Water does not form a stable enough complex with the hydroxyl groups to destroy the hydrogen bonding. The problem of putting cellulose into solution in aqueous media without formation of derivatives with primary valence bonds thus resolves itself into the search for reagents which have a strong tendency to form coordination compounds with hydroxyl groups.

A wide variety of such reagents is available. The strong mineral acids dissolve cellulose in certain concentration ranges.[12] This may be presumed to be due to the formation of the $—OH_2^+$ ion attached to the cellulose. As the hydroxyls of the cellulose must compete with water for the hydrogen ion, solubility of cellulose in acids occurs only in concentrations high enough to have an appreciable activity of unionized acid. For example, with HCl this occurs at the point where the partial pressure of HCl gas is nearly one atmosphere. With H_2SO_4, solubility is best in the 72% acid, where there is only a slight excess of water above that necessary to combine with both hydrogens of the acid. It is interesting to note that the activity of water is about the same at the optimum concentrations of all the mineral acids, as well as of the salts and bases which dissolve cellulose. Solutions of cellulose in acid degrade very rapidly at ordinary temperature, but, at low temperatures, fairly stable solutions may be obtained. Seemingly, cellulose of any chain length may be dissolved in HCl or H_2SO_4 solutions, but only the lower-molecular-weight products are soluble in H_3PO_4 solutions.

Cellulose has some tendency to dissolve in concentrated solutions of those salts which are very soluble in water and alcohols.[75] Possibly the best salt solvent is a solution of basic beryllium perchlorate.[76] Other salt solutions dissolve only cellulose which is more or less degraded. The degree of solvent power follows the usual lyotropic series, increasing in the order Cl, NO_3, Br, I, SCN; Ba, Sr, Ca, Mg; and K, NH_4, Na, Li.[77]

Zinc chloride is the only salt used commercially as a cellulose solvent. This salt (72%) swells cellulose fibers, dissolving only the lower-molecular-weight portions. The commercial vulcanized fiber process involves swelling paper in $ZnCl_2$ solutions, pressing the sheets together or winding them on a mandrel to form a tube, leaching out the salt, and drying.

The most useful cellulose solvents are alkaline in nature. Sodium hydroxide, about the best solvent among the inorganic bases, exhibits its maximum solvent power at a concentration of about 2 *N* and a temperature just above the freezing point.[78] As the temperature is raised, the solubility is decreased, and the optimum concentration of NaOH necessary is increased. This is, of course, good evidence that some sort of addition compound is formed, its formation being promoted by lower temperature.

The existence of an optimum concentration is very characteristic of the alkaline solvents, as it is with salts and acids. The higher concentrations have, of course, a greater tendency to form addition compounds, but they also have a considerable salting-out tendency. With sodium hydroxide, x-ray studies show that compound formation is just beginning at the concentration of maximum solubility.

There are two methods by which the salting-out tendency at high concentrations of ionizing bodies can be counteracted. One of these is to make use of compounds which, for a given degree of combination with the cellulose, will loosen its structure to the maximum extent. Such compounds are the high-molecular-weight, strong organic bases, such as tetraethylammonium hydroxide or dibenzyldimethylammonium hydroxide. (See Chapter VIII, D, 4 for a bibliography on this topic.) Lieser[79] has pointed out that the solvent power of these bases is connected with their molecular volume. The larger the molecule, the further apart the

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[75] A review of work on this subject is given by H. Erbring and H. Geinitz, *Kolloid-Z.*, **84**, 25 (1938); see also J. R. Katz and J. Seiberlich, *Paper Trade J.*, **110**, 37 (Feb. 15, 1940); G. S. Kasbekar, *Current Sci.*, **9**, 411 (1940).

[76] A. Dobry, *Bull. soc. chim.*, [5], **3**, 312 (1936).

[77] D. J. Gerritsen, *Chem. Weekblad*, **33**, 405 (1936); *Chem. Zentr.*, **1936, II**, 1934.

[78] G. F. Davidson, *J. Textile Inst.*, **27**, T112 (1936).

[79] T. Lieser, *Ann.*, **528**, 276 (1937).

chains are pushed and the greater the loosening of the cellulose structure for a given degree of combination. The organic bases are similar to the inorganic in that the concentration range for maximum solubility is rather limited and is in the neighborhood of 2 *N*. The lower limit of concentration for solution decreases as the molecular volume of the base increases.

Obviously, if a stronger bond is formed between the cellulose and some ingredient in the solvent, solution will occur at a lower concentration. No solvent depending for its activity solely on the addition of hydroxyl ion to the cellulose can be expected to dissolve cellulose at concentrations much less than 1.5 *N*. The enhanced solubility of cellulose in solutions of sodium hydroxide in which beryllium hydroxide has been dissolved[80] is probably due to formation of a complex between the beryllium and the cellulose.

Until the discovery of the solvent power of the strong organic bases, the only satisfactory cellulose solvents contained ammonia or an amine, and copper hydroxide. The chemistry of these complexes has already been reviewed in Chapter VIII, Section D, 3. The often-stated assumption that the solubility of cellulose in cuprammine solutions is due to their strong basicity is not well founded, as they dissolve cellulose at much lower concentrations than do the typical strong bases. It has been shown by Jolley[81] (see also Chapter VIII, D, 3) that in cupri-ethylenediamine complexes the copper is linked to the cellulose. This is probably true in cuprammonium solutions also, but nothing is known of the mode of linkage.

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[80] G. F. Davidson, *J. Textile Inst.*, **28**, T27 (1937).

[81] L. J. Jolley, *J. Textile Inst.*, **30**, T22 (1939).

B. THERMODYNAMIC PROPERTIES OF SOLUTIONS OF LONG-CHAIN COMPOUNDS

MAURICE L. HUGGINS

1. Some General Thermodynamic Relationships

The thermodynamic properties of a solution can be most conveniently treated in terms of the activities, a_1, a_2 . . ., of its components. The activity is defined as the fugacity or "escaping tendency" relative to that of the pure liquid component.

For equilibrium between the solution and another phase—gas, solid, liquid, solution—containing a given component, the activity of this component must be the same in both phases. From this requirement, the following relationships, among others, can be deduced:

(1) The vapor pressure of a component of a solution equals its activity in the solution times the vapor pressure of the pure liquid component (provided the vapor obeys the ideal gas laws):

$$p_1 = a_1 p_1^0 \tag{1}$$

(2) The lowering of the freezing point of a liquid (component 1) by the addition of a solute (component 2) is given by the equation

$$\vartheta_f = -\frac{RT^2_{f,1}}{\Delta H_{f,1}} \ln a_1 \tag{2}$$

where R is the gas constant (1.986 cal. deg.$^{-1}$ mole^{-1}), $T_{f,1}$ is the absolute temperature of the freezing point of the pure liquid solvent, and $\Delta H_{f,1}$ is its molal heat of fusion.

(3) Similarly, for the elevation of the boiling point,

$$\vartheta_b = -\frac{RT^2_{b,1}}{\Delta H_{v,1}} \ln a_1 \tag{3}$$

$T_{b,1}$ and $\Delta H_{v,1}$ are the boiling point and the heat of vaporization of the solvent, respectively.

(4) The osmotic pressure of a solution depends on the activity of the solvent according to the equation

$$\Pi = -\frac{RT}{\bar{V}_1} \ln a_1 \tag{4}$$

$\bar{V}_1$ is the partial molal volume of the solvent. R is again the gas constant; its numerical value depends on the units in which Π and $\bar{V}_1$ are expressed.

Thermodynamics also gives us the relation

$$N_1 \left(\frac{\partial \ln a_1}{\partial N_1} \right) - N_2 \left(\frac{\partial \ln a_2}{\partial N_2} \right) = 0 \tag{5}$$

between the activities and mole fractions of the components of a binary solution. If the activity-concentration curve for one component (or an algebraic expression for it) is known, that for the other can thus be deduced.

It is obvious from the relationships just given that, from a knowledge of the dependence of the activity of either component of a binary solution on the concentration or the nature of the components or the temperature, etc., the dependence on the same variable of the vapor pressure, the osmotic pressure, the freezing-point lowering, etc., can readily be determined.

The activity of component 1 of a solution is related by thermodynamics to its partial molal heat of mixing ($\bar{L}_1$) and entropy of mixing ($\Delta\bar{S}_1$) according to the equation

$$\ln a_1 = \frac{\bar{L}_1}{RT} - \frac{\Delta\bar{S}_1}{R} \tag{6a}$$

Likewise, for component 2,

$$\ln a_2 = \frac{\bar{L}_2}{RT} - \frac{\Delta\bar{S}_2}{R} \tag{6b}$$

2. Certain Approximate Relations of Limited Applicability

The heat of mixing depends on the relative attraction energies of *like* molecules and of *unlike* molecules in the solution. Roughly speaking, a positive value of $\bar{L}_1$ means that a molecule of component 1 prefers to be surrounded entirely by other molecules of the same kind, rather than by a mixture of molecules of types 1 and 2. With the aid of certain reasonable approximations, one can deduce the equations[1–3]

$$\bar{L}_1 = K\bar{V}_1 V_2^2 \tag{7a}$$

and

$$\bar{L}_2 = K\bar{V}_2 V_1^2 \tag{7b}$$

where V_1 and V_2 are the volume fractions of the components and K is a constant whose magnitude depends on the nature of both components.

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[1] J. J. van Laar, *Z. physik. Chem.*, **A137**, 421 (1928).
[2] G. Scatchard, *Chem. Revs.*, **8**, 321 (1931).
[3] J. H. Hildebrand, *J. Am. Chem. Soc.*, **57**, 866 (1935).

On theoretical grounds, it would be expected that equations (7a) and (7b) would be approximately true over a considerable concentration range for many solutions, but certainly not for all. (Space cannot be taken here to discuss the requirements for their validity or the form of the relationships when these equations are inapplicable.) The experimental measurements are in agreement with this expectation.

Entropy is a measure of randomness. The simple case of a solution composed of two kinds of molecules, both spherical, of the same size and alike as regards their attractions and repulsions for other molecules, can be treated by the methods of statistical mechanics. The number of possible distributions of the two molecular species among the available sites can be computed as a function of the composition. Assuming all these alternatives to be equally probable, the entropies of mixing are computed[4] to be

$$\Delta\bar{S}_1 = -R \ln N_1 \tag{8a}$$

and

$$\Delta\bar{S}_2 = -R \ln N_2 \tag{8b}$$

Substitution into equations (6a) and (6b) gives, for $\bar{L}_1$ and $\bar{L}_2$ equal to zero,

$$a_1 = N_1 \tag{9a}$$

and

$$a_2 = N_2 \tag{9b}$$

These represent Raoult's law. Empirically, this law is found to hold approximately for many binary solutions for which there is little or no heat of mixing—evidence that the entropy of mixing *for mutual solutions of ordinary small molecules* is nearly independent of their size and shape.

If the heat of mixing is not negligible, the assumption, underlying equations (8a) and (8b), that all distributions of the two kinds of molecules in the solution are equally probable, is not true; hence these equations are certainly inaccurate. If, nevertheless, they are used as a first approximation, equations (7a) and (7b) for the activities of the components of a (small-molecule) solution become

$$\ln a_1 = \ln N_1 + \left(\frac{K\bar{V}_1}{RT}\right) V_2^2 \tag{10a}$$

and

$$\ln a_2 = \ln N_2 + \left(\frac{K\bar{V}_2}{RT}\right) V_1^2 \tag{10b}$$

[4] R. H. Fowler and G. S. Rushbrooke, *Trans. Faraday Soc.*, **33**, 1272 (1937).

3. The Activities in Solutions of Long-Chain Compounds

For solutions of long-chain compounds, these equations do not hold at all well. This is illustrated by Figure 11, which shows the variation of a_1 with

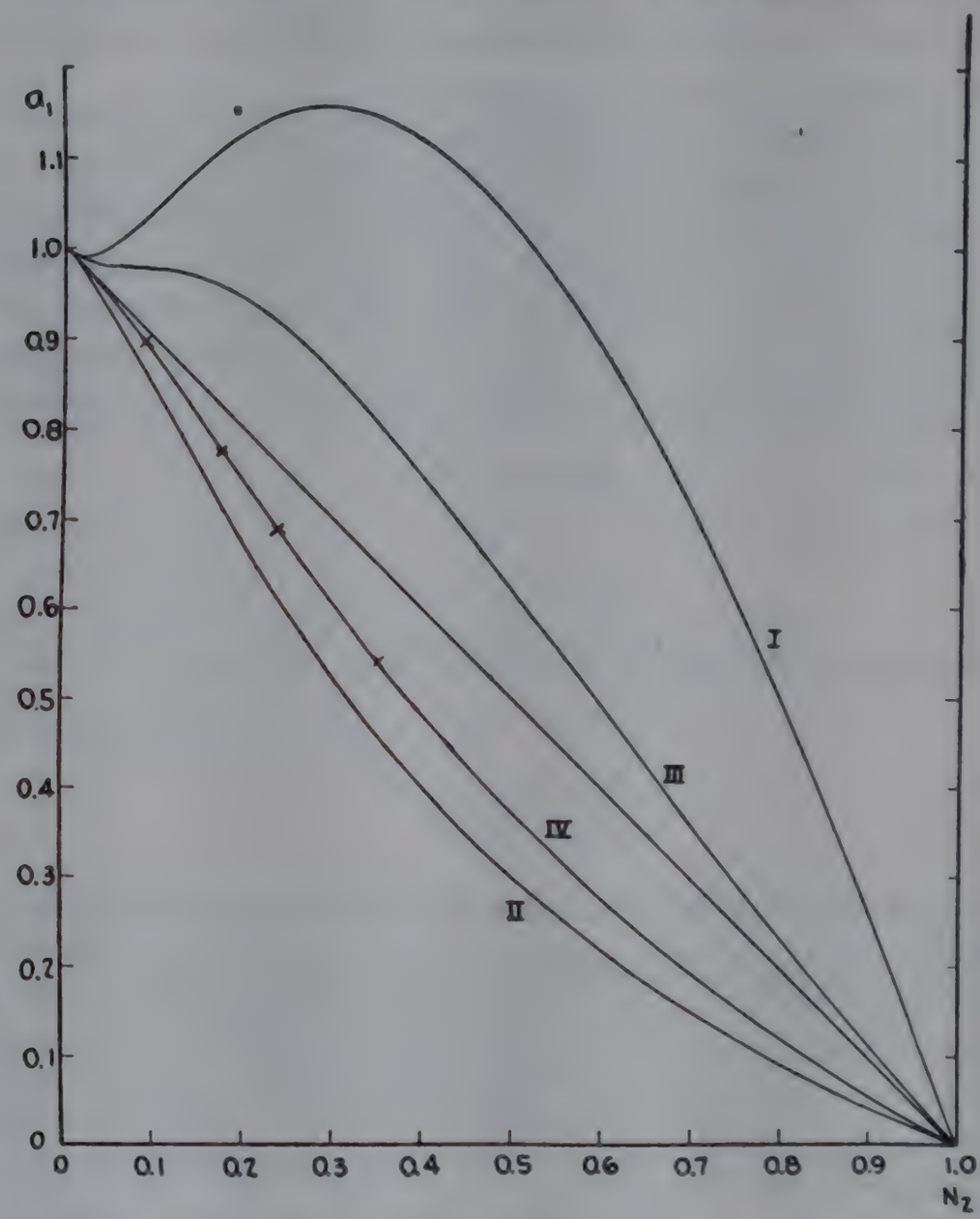

FIG. 11.—ACTIVITY VERSUS MOLE FRACTION FOR SOLUTIONS OF OLEYL OLEATE IN CYCLOHEXANE (MEYER AND LÜHDEMANN[5]).

$\bar{V}_2/\bar{V}_1 = 5.7$. The straight line represents Raoult's law (equation (9a)). Curve I represents equation (10a). Curves II, III, and IV represent equation (11a), with μ_1 equal to 0, 1.0 (from the heat of mixing), and 0.29 (empirical), respectively.

mole fraction for one of several systems studied by Meyer and Lühdemann.[5] The straight line with a 45° slope represents Raoult's law.

[5] K. H. Meyer and R. Lühdemann, *Helv. Chim. Acta*, **18**, 307 (1935).

Curve I, representing equation (10a) (with K calculated from the experimental heat of mixing measurements), deviates very markedly from Curve IV, which passes through the experimental points. Similar large deviations are shown for other systems for which good experimental data have been obtained.[6]

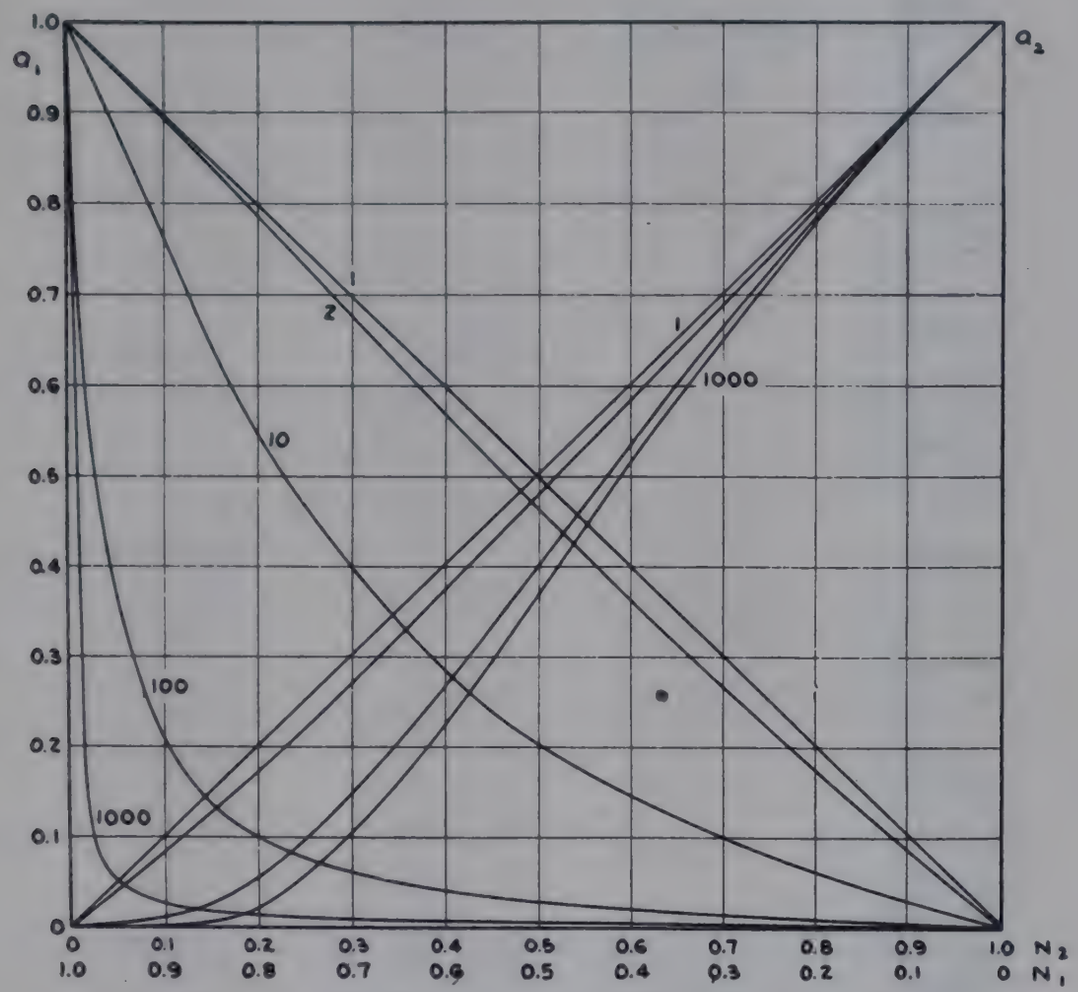

FIG. 12.—THEORETICAL CURVES OF ACTIVITY VERSUS MOLE FRACTION, ACCORDING TO EQUATIONS (10a) AND (10b), WITH $\mu_1 = \mu_2 = 0$.

The numbers alongside the curves indicate the ratio $\bar{V}_2/\bar{V}_1$. The unnumbered curves for a_2 are for $\bar{V}_2/\bar{V}_1$ equal to 2 and 10.

For high polymers, natural or synthetic, the deviations from equations (10a) and (10b) are even greater, always indicating much lower activities than would be expected from these relations. As pointed out by Meyer,[7] equations (8a) and (8b) must be inapplicable to such systems. From qualitative considerations, he has shown that one should expect large

[6] M. L. Huggins, *Annals N. Y. Acad. Sciences*, **43**, 1 (1942).

[7] K. H. Meyer, *Helv. Chim. Acta*, **23**, 1063 (1940).

deviations, in the right direction to explain the experimental results, for solutions of irregularly kinked chain molecules.

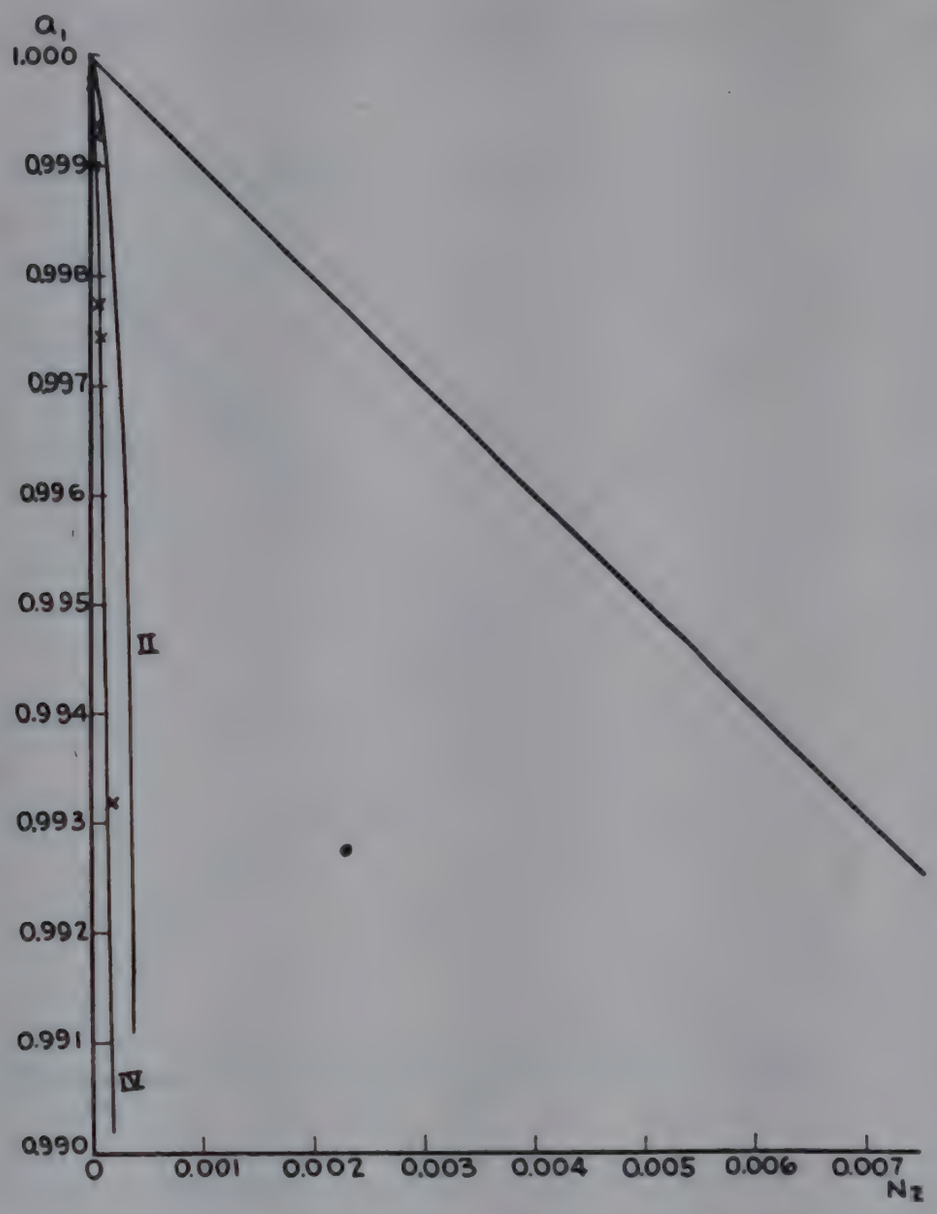

FIG. 13.—VARIATION OF ACTIVITY WITH MOLE FRACTION FOR SOLUTIONS OF CELLULOSE TRIACETATE IN TETRACHLOROETHANE, FROM OSMOTIC PRESSURE DATA (HAGGER AND VAN DER WYK[8]).

Curves II and IV represent equation (11a), with μ_1 equal to 0 and −3.0 (empirical), respectively.

A quantitative calculation of the entropy of mixing for such solutions has been carried out independently by Flory[9] and by Huggins.[6, 10] From

[8] O. Hagger and A. J. A. van der Wyk, *Helv. Chim. Acta*, **23**, 484 (1940).
[9] P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).
[10] M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942).

their results, using the latter's terminology, equations (10a) and (10b) should be replaced by

$$\ln a_1 = \ln V_1 + \left(1 - \frac{\bar{V}_1}{\bar{V}_2}\right) V_2 + \mu_1 V_2^2 \tag{11a}$$

and

$$\ln a_2 = \ln V_2 + \left(1 - \frac{\bar{V}_2}{\bar{V}_1}\right) V_1 + \mu_2 V_1^2 \tag{11b}$$

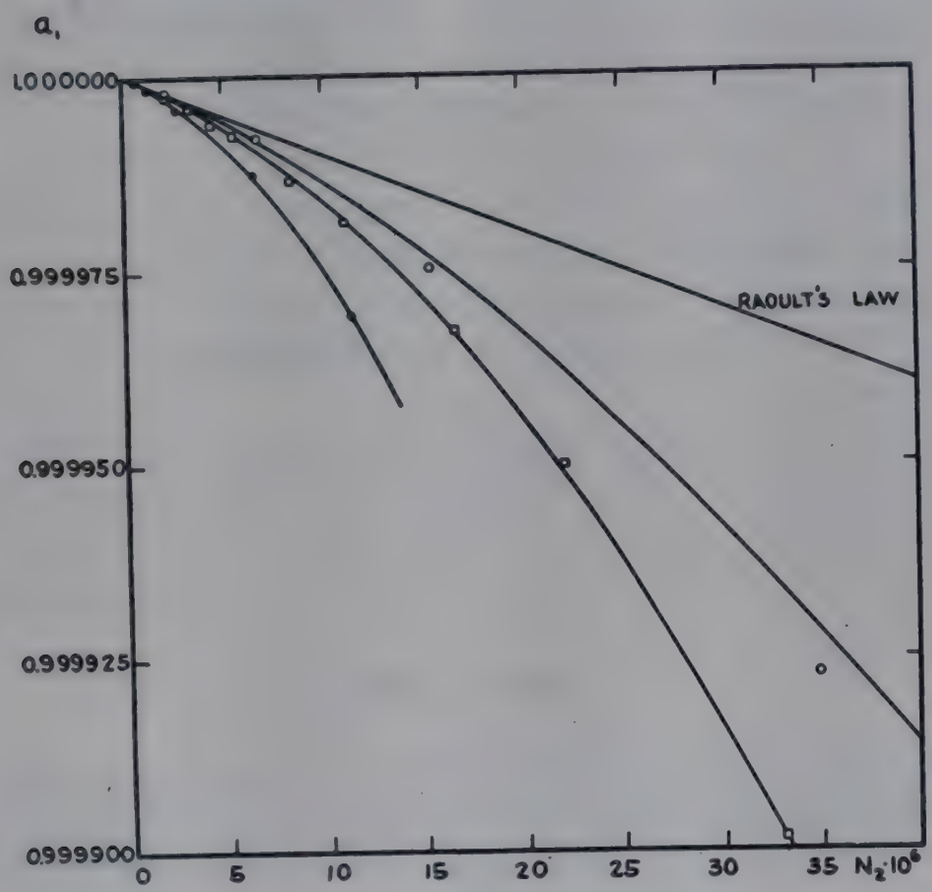

FIG. 14.—ACTIVITY VERSUS MOLE FRACTION FOR SOLUTIONS OF CELLULOSE NITRATE IN ACETONE, FROM OSMOTIC PRESSURE DATA ON THREE SAMPLES WHICH DIFFERED WITH REGARD TO THE DEGREE OF NITRATION, THE AVERAGE CHAIN LENGTH, AND THE TEMPERATURE.

● Dobry[11] ($\mu_1 = 0.265$; $V_2/V_1 = 793$; $t = 22°$).
□ Schulz[12] ($\mu_1 = 0.300$; $V_2/V_1 = 550$; $t = 27°$).
O Duclaux and Wollman[13] ($\mu_1 = 0.19$; $V_2/V_1 = 330$; $t = 20°$).

To agree with equation (5), μ_1 and μ_2 must be related by the equation

$$\mu_1 \bar{V}_2 = \mu_2 \bar{V}_1 \tag{12}$$

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[11] A. Dobry, *J. chim. phys.*, **32**, 50 (1935).
[12] G. V. Schulz, *Z. physik. Chem.*, **A176**, 317 (1936).
[13] J. Duclaux and E. Wollman, *Compt. rend.*, **152**, 1580 (1911).

μ_1 (and so also μ_2) is approximately constant, independent of concentration, for a given system. Its magnitude depends on the heats of mixing (compare equations (7a) and (7b)) and also on the shapes and flexibilities of the molecules, the departure from perfect randomness of mixing, and other factors. (Only the heat of mixing contribution was considered by Flory; the other factors are, however, by no means negligible.)

Figure 12 shows activity versus mole fraction curves, conforming to equations (11a) and (11b), for various values of the ratio $\bar{V}_2/\bar{V}_1$, μ_1 and μ_2 being taken equal to zero throughout. It is evident that, for high-polymer solutions ($\bar{V}_2/\bar{V}_1$ large), the deviations from Raoult's law (represented by the straight lines labeled "1") should be very large.

Equations (11a) and (11b) have been tested[6, 14] with data on many different kinds of solutions and have been found to represent the experimental results adequately. The agreement is illustrated by Figures 13 and 14, representing the variation of solvent activity with mole fraction, for solutions of cellulose acetate in tetrachloroethane[8] and of cellulose nitrate in acetone.[11, 12, 13]

In these and similar comparisons of experimental data with the theoretical equations given here, it has been necessary to assume additivity of molal volumes ($\bar{V}_1 = V_1$; $\mathcal{V}_1 = N_1V_1/(N_1V_1 + N_2V_2)$; etc.). It is believed that this approximation has not led to any significant error.

4. Osmotic Pressure

The following relation between osmotic pressure and concentration ($\mathcal{V}_2$) is obtained by combining equations (4a), (4b), and (11a), expanding $\ln \mathcal{V}_1$ in powers of $\mathcal{V}_2$, and dropping all terms in this expansion after the third

$$\frac{\Pi}{\mathcal{V}_2} - \frac{RTV_2^2}{3\bar{V}_1} = \frac{RT}{\bar{V}_2} + \frac{RT}{\bar{V}_1}\left(\frac{1}{2} - \mu_1\right)\mathcal{V}_2 \tag{13}$$

For concentrations (C_2) in grams of solute per cubic centimeter of solution,

$$\frac{\Pi}{C_2} - \frac{RTC_2^2}{3\bar{V}_1 d_2^2} = \frac{RT}{M_2} + \frac{RT}{\bar{V}_1 d_2^2}\left(\frac{1}{2} - \mu_1\right)C_2 \tag{14}$$

M_2 and d_2 denote the molecular weight and density of the solute. Similar equations can of course be written for concentrations in other units.

In the concentration range in which osmotic pressures are usually

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[14] M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 1712 (1942).

measured, the second term on the left in each of the last two equations is negligible or nearly so. Hence,

$$\frac{\Pi}{C_2} \approx a + bC_2 \tag{15}$$

where a and b are both constant for a given system. This agrees with the well-known empirical fact[15] that, if the ratio of osmotic pressure to concentration is plotted against the concentration, the experimental points fall on or near a straight line.

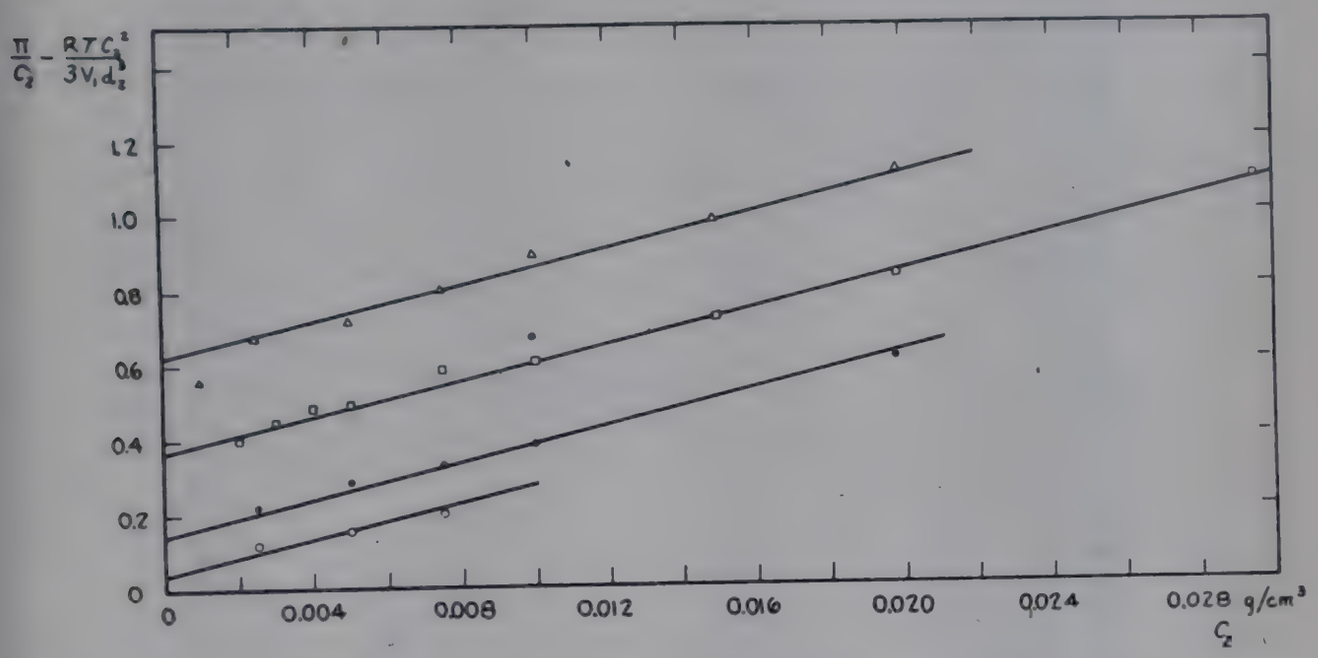

FIG. 15.—DEPENDENCE OF OSMOTIC PRESSURE ON CONCENTRATION FOR ACETONE SOLUTIONS OF DIFFERENT FRACTIONS OF A CERTAIN CELLULOSE NITRATE PREPARATION AT 27°C. (SCHULZ[12]).

The straight lines represent equation (14), with $\mu_1 = 0.300$.

Figure 15 shows the agreement with equation (14) for solutions in acetone of several fractions of a cellulose nitrate preparation.[12] The intercepts on the ordinate axis are inversely proportional to the average molecular weights. The slopes of the lines for the different fractions are the same, as would be expected, since, for long-chain molecules built up of identical units, μ_1 would be expected to be independent of chain length.

For the dependence of freezing-point lowering and boiling-point elevation on concentration, equations (2) and (3) obviously can be used, instead of (4), to obtain relations similar to (13) and (14).

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[15] H. Mark, *High Polymers*, Vol. II, *Physical Chemistry of High Polymeric Systems* Interscience, New York, 1940.

5. Separation into Two Phases. Gels

The effect of the magnitude of μ_1 on the activity-concentration curves is shown in Figures 16, 17, and 18.

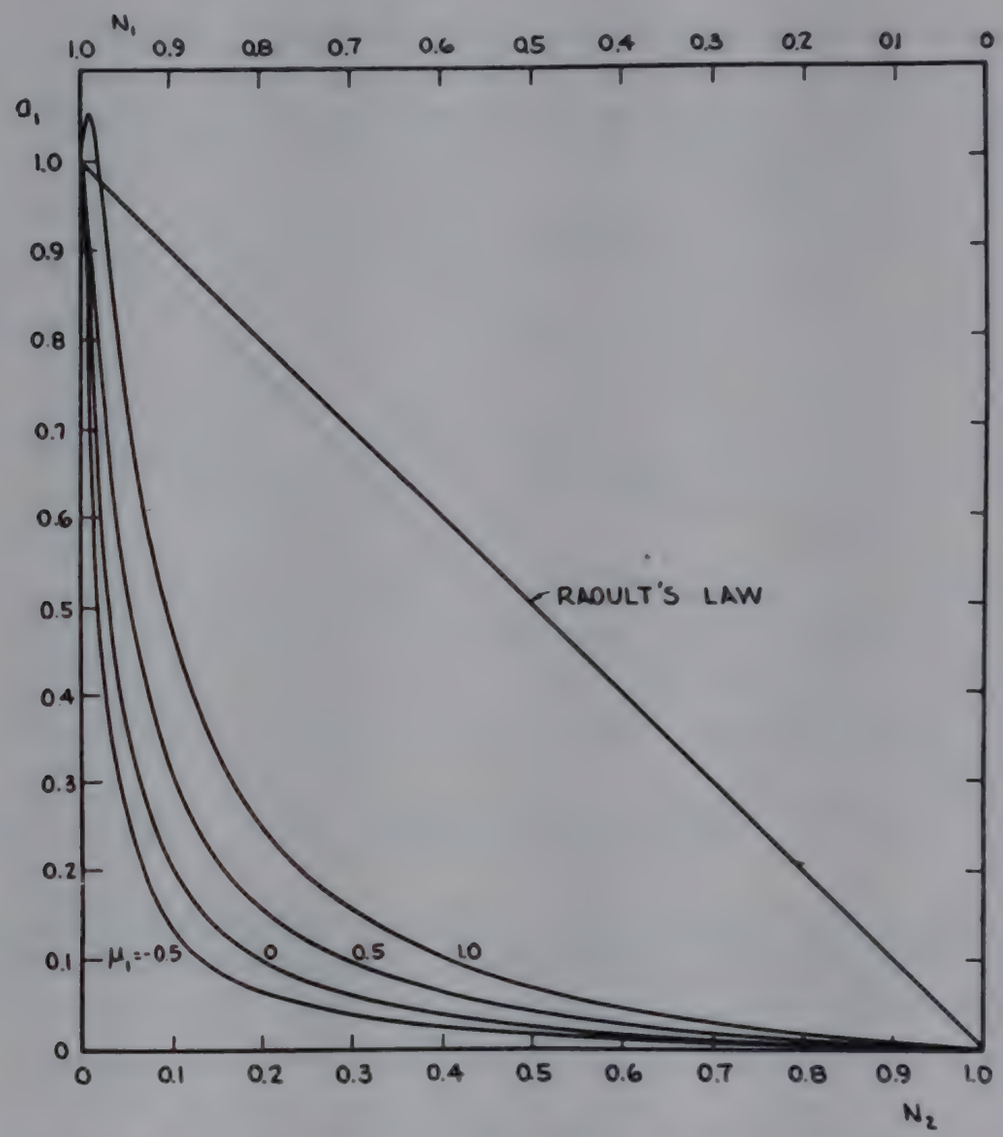

FIG. 16.—ACTIVITY (a_1) VERSUS MOLE FRACTION, ACCORDING TO EQUATION (11a), FOR $\bar{V}_2/\bar{V}_1 = 100$, WITH CERTAIN VALUES OF μ_1.

In the first of these, which is drawn for a ratio of molal volumes equal to 100, the concentrations are in mole fractions, as in Figures 11 to 14. In the other two, the concentrations are in volume fractions. In Figure 18, curves for $\bar{V}_2/\bar{V}_1$ equal to 100 or any larger number would be scarcely distinguishable from those shown, which were calculated for this ratio equal to infinity.

The occurrence of a minimum and a maximum in an activity-concentration curve (see, especially, Fig. 17) indicates a separation into two phases.

For each component the activity must be the same in both phases. By combining this requirement with equations (11) and (12), the compositions of the two phases and the activities of the components may be computed

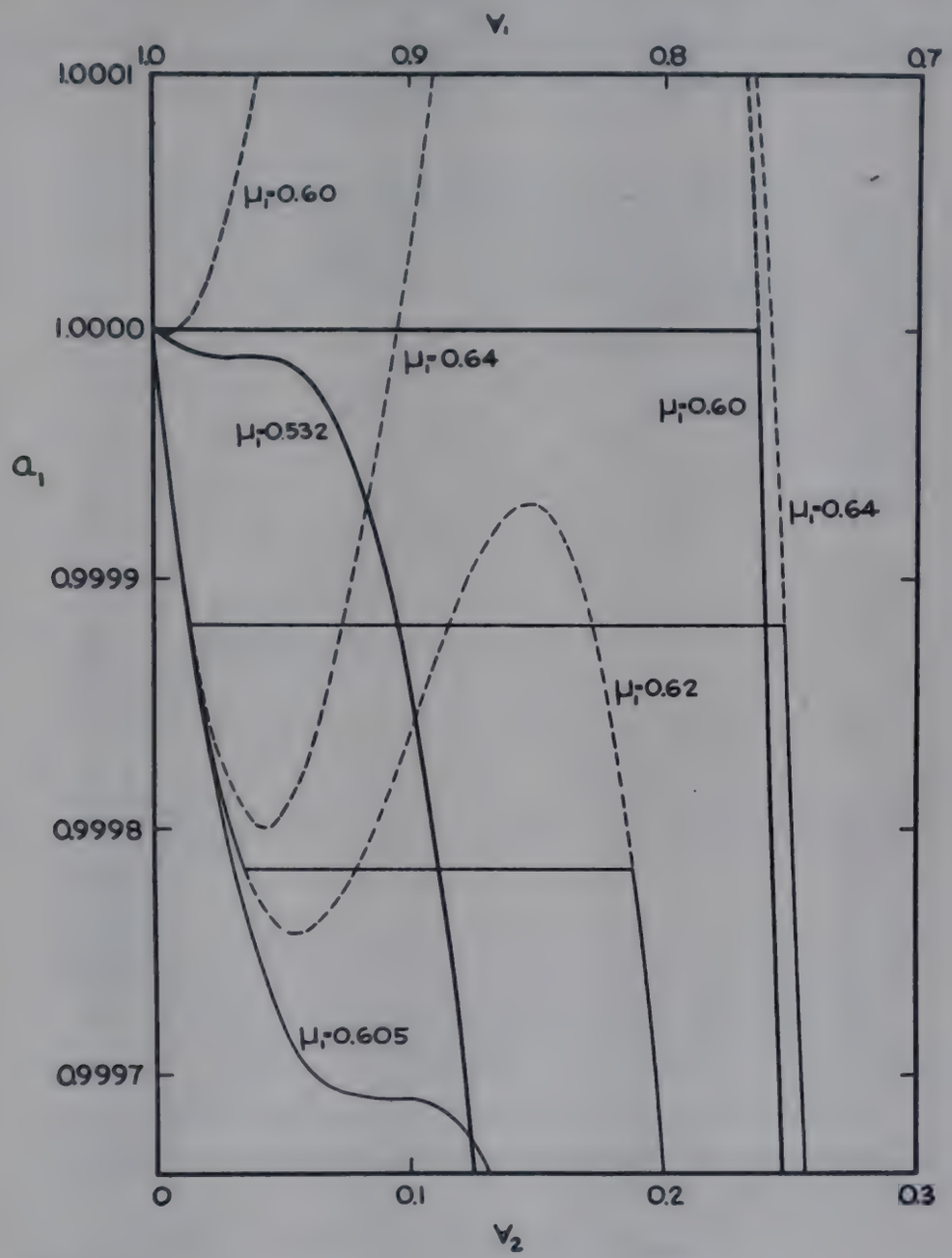

FIG. 17.—ACTIVITY (a_1) VERSUS VOLUME FRACTION, ACCORDING TO EQUATION (11a), FOR $\bar{V}_2/\bar{V}_1 = 100$ (LIGHTER LINES) AND 1000 (HEAVIER LINES), AND CERTAIN VALUES OF μ_1.

for any given μ_1 and volume ratio. The positions of the horizontal lines in Figure 17 and the curves of Figure 19, showing the compositions of the phases as functions of μ_1, were obtained in this way.

For systems consisting of small molecules and very large molecules, the following generalizations hold.

(1) The activity of the small molecule component is only slightly less than unity in both phases. (For $\bar{V}_2/\bar{V}_1 = 1000$, $a_1 \geqq 0.99999$; see Fig. 17.)

(2) One phase consists almost entirely of the small molecule component. (For $\bar{V}_2/\bar{V}_1 = 1000$, $V_1 \geqq 0.97$; see Figs. 17 and 19.)

(3) The composition of the other phase is approximately that given by the intersection, at largest N_2 or V_2 value, of the horizontal line (in an

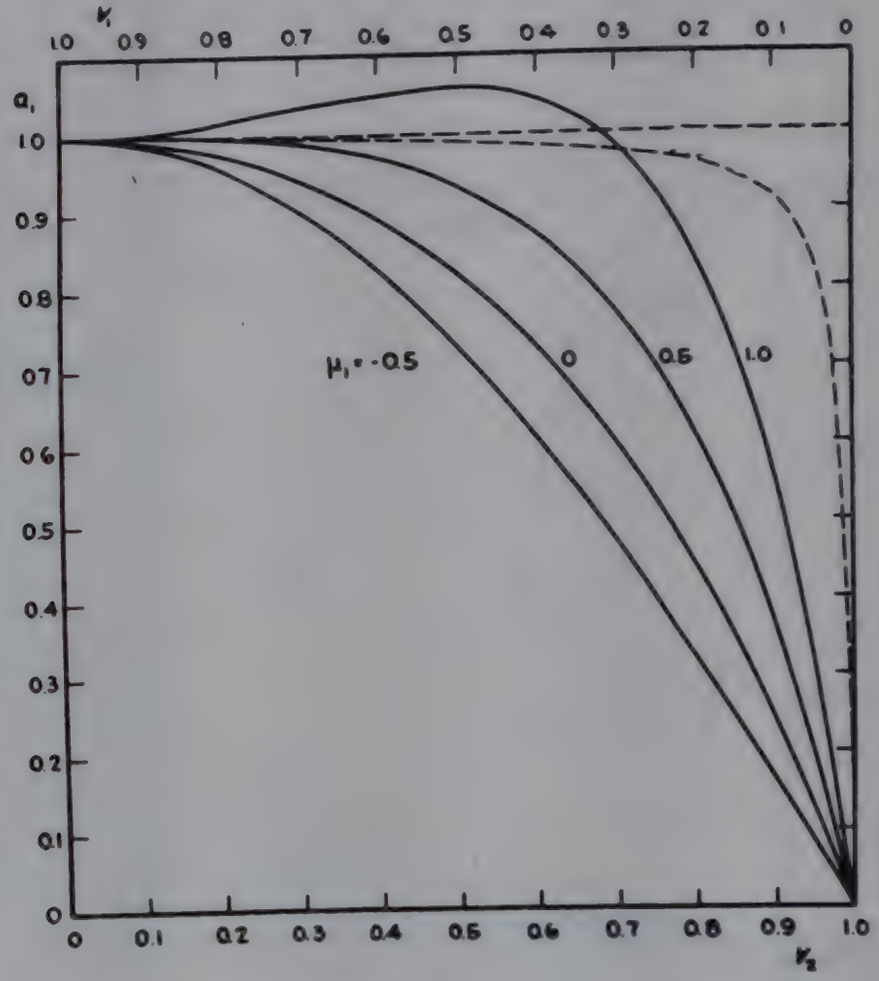

FIG. 18.—ACTIVITY (a_1) VERSUS VOLUME FRACTION, ACCORDING TO EQUATION (11a), FOR $\bar{V}_2/\bar{V}_1 = \infty$, WITH CERTAIN VALUES OF μ_1.

The dashed horizontal line and curve represent Raoult's law for $\bar{V}_2/\bar{V}_1 = \infty$ and 100, respectively.

a_1 versus N_2 or a_1 versus V_2 graph, such as Fig. 18) representing $a_1 = 1$ with the activity curve, except for values of μ_1 very near the critical value. (For $\bar{V}_2/\bar{V}_1 = 1000$, with $\mu_1 \geqq 0.540$, this approximation produces an error in V_2 of less than 0.005.)

(4) The composition of the phase richer in the high-molecular-weight component varies but little with the molecular weight of that component (or, better, with the molal volume ratio), again excepting systems for

which μ_1 is near the critical value. (Compare the curves for $\bar{V}_2/\bar{V}_1 = 1000$ and $\bar{V}_2/\bar{V}_1 = \infty$, Fig. 19.)

The critical value of μ_1, above which the mixture should separate into two phases, depends on the ratio of the partial molal volumes according to the equation[16]

$$\mu_1(\text{crit.}) = \frac{1}{2}\left[1 + \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{1/2}\right]^2 \tag{16}$$

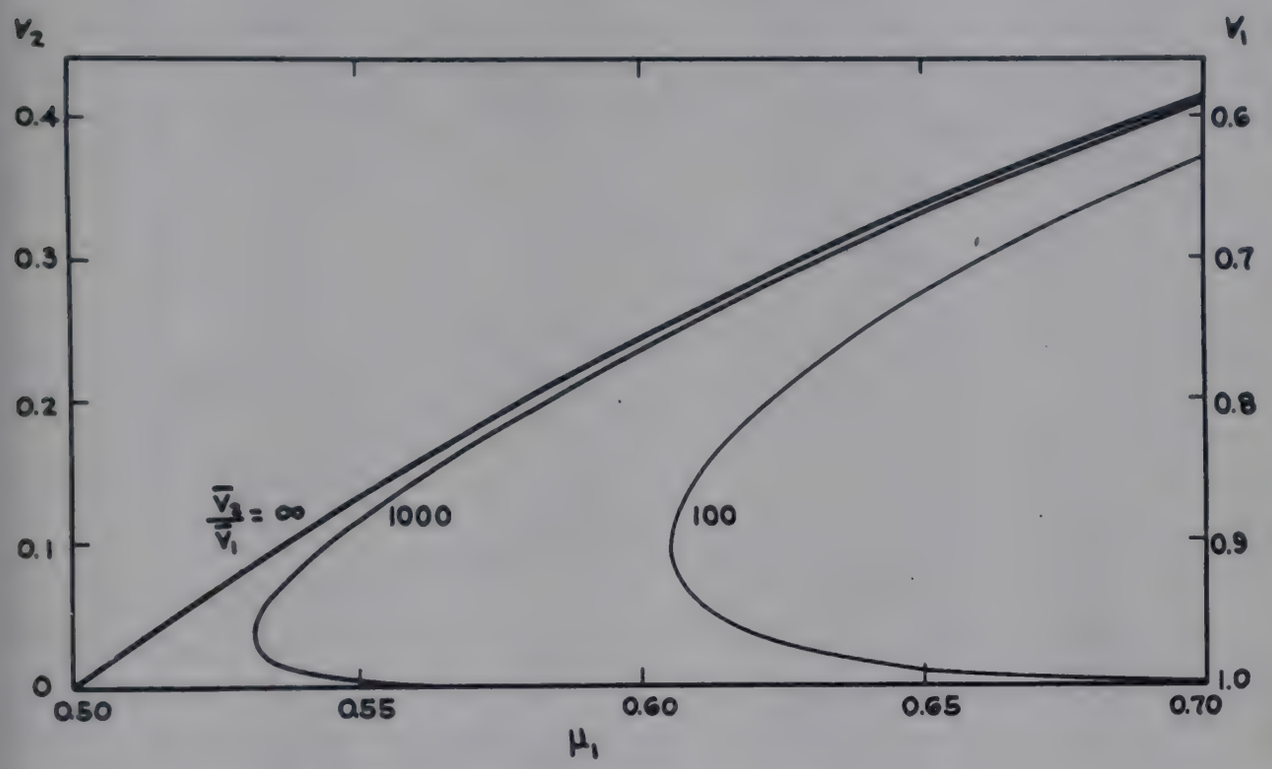

FIG. 19.—DEPENDENCE ON μ_1 OF THE COMPOSITIONS OF TWO PHASES IN EQUILIBRIUM WITH EACH OTHER, FOR $\bar{V}_2/\bar{V}_1 = 100$, 1000, AND ∞.

This dependence is shown graphically in Figure 20. If one component has a high molecular weight (and, so, molecular volume) relative to that of the other component, the critical value of μ_1 is very close to one-half.

Solutions of long-chain molecules in solvents with small molecules, in which the former are present in moderate or high concentration, have high viscosities, partly because of mutual interference of the long chains. This is especially true if the chains tend to adhere to each other when in contact, as is the case when the heat of mixing (and so μ_1) has a large positive value, causing the mixture to separate into two phases. The phase richer in the high-molecular-weight component thus usually has the properties of a gel; it may be considered as a single flexible network molecule containing small molecules interspersed between the threads of the net. ($\bar{V}_2/\bar{V}_1 \approx \infty$.)

[16] P. J. Flory, *J. Chem. Phys.*, **9**, 660 (1941).

Careful consideration of the details of the assumptions involved in the derivation of equations (11a) and (11b), moreover, shows that they should hold, at least approximately, not only for solutions of unbranched chain-molecules but also for systems containing branched chain-molecules or flexible network molecules. These equations thus provide a sound theoretical basis for a quantitative treatment of the equilibrium properties of

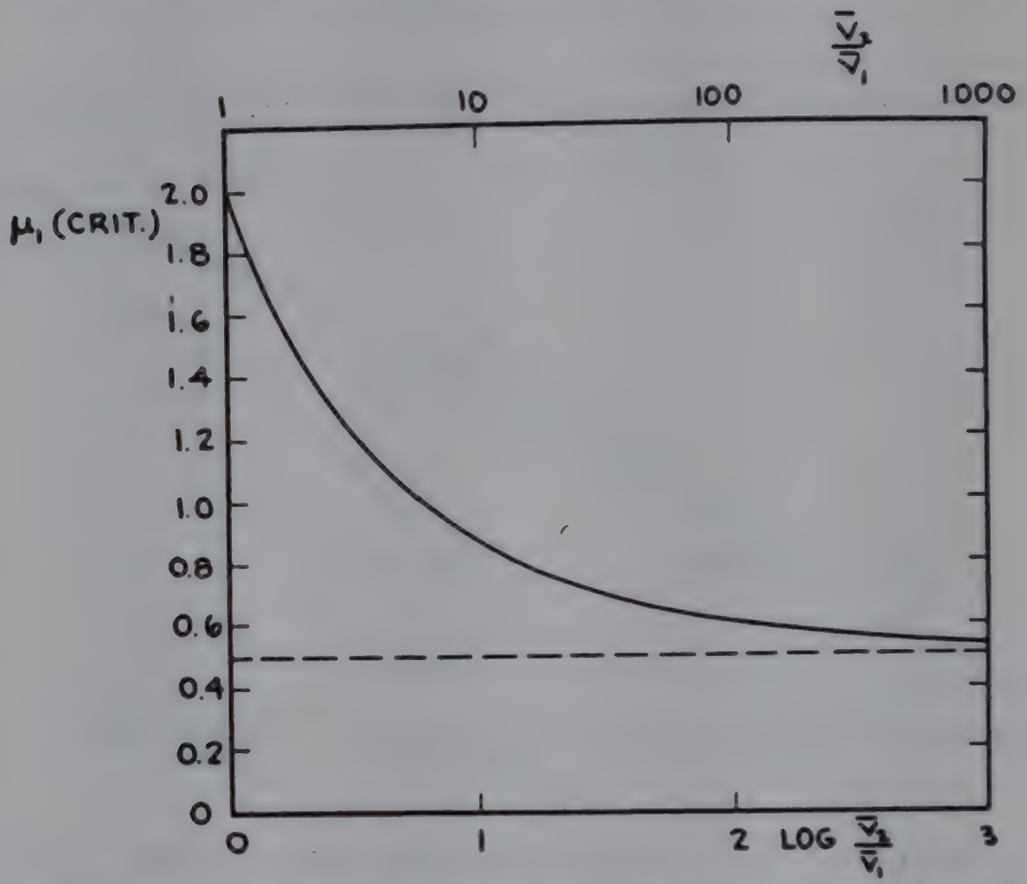

FIG. 20.—DEPENDENCE ON THE (PARTIAL) MOLAL VOLUME RATIO OF THE CRITICAL VALUE OF μ_1 FOR SEPARATION OF A SOLUTION INTO TWO PHASES, ACCORDING TO EQUATION (16).

gels. Such comparisons with experiment as have been made verify this statement.

If the final term in equation (11a) were due entirely to the heat of mixing, it would be expected, from equations (6a) and (7a), that μ_1 would be roughly proportional to $\bar{V}_1/T$ (and so to V_1/T). As noted above, however, other factors are involved. For polystyrene-alkyl laurate gels,[14, 17] μ_1 depends on temperature and on V_1 approximately according to the equation

$$\mu_1 = \alpha_1 + \frac{\gamma_1 + \delta_1 V_1}{T} \tag{17}$$

[17] J. N. Brønsted and K. Volqvartz, *Trans. Faraday Soc.*, **35**, 576 (1939).

with α_1 and γ_1 having negative values and δ_1 positive. A similar relation, but with different values of the constants, may be expected to hold for other systems.

6. Solubility of High-Molecular-Weight Solid Compounds

Considering now the solubility at a given temperature of a pure high-molecular-weight solid in a low-molecular-weight liquid, use is made of the thermodynamic requirement that the logarithm of the activity of the high-molecular-weight component in the solution must equal the negative of the hypothetical free energy change on fusion at the temperature in question, divided by RT:

$$\ln a_2 = -\frac{\Delta F_{f,2}}{RT} = \frac{\Delta H_{f,2}}{R}\left(\frac{1}{T_{f,2}} - \frac{1}{T}\right) = \frac{\Delta S_{f,2}}{R} - \frac{\Delta H_{f,2}}{RT} \tag{18}$$

$\Delta H_{f,2}$, $\Delta S_{f,2}$, and $T_{f,2}$ represent the heat of fusion, entropy of fusion, and melting point (°K.), respectively, of pure component 2.

For very long chains,

$$\Delta F_{f,2} = \frac{V_2}{V_1} f_2 \tag{19}$$

where f_2 is a constant, equal to the free energy of fusion of a volume of component 2 equal to V_1. The combination of equations (11b), (12), (18), and (19) (neglecting the difference between $\bar{V}_2/\bar{V}_1$ and V_2/V_1) gives

$$\ln V_2 = \frac{V_2}{V_1}\left[\left(V_1 - \frac{f_2}{RT}\right) - \mu_1 V_1^2\right] \tag{20}$$

If the solubility is small, V_1 is approximately unity and

$$\ln V_2 \approx -\frac{V_2}{V_1}\left(\frac{f_2}{RT} + \mu_1\right) \tag{21}$$

or

$$V_2 \approx \exp\left[-\frac{V_2}{V_1}\left(\frac{f_2}{RT} + \mu_1\right)\right] \tag{22}$$

Thus, for a homologous series of chain compounds which are only slightly soluble in a given solvent, the solubility decreases exponentially as the chain length (proportional to V_2/V_1) increases.

For the special case of a mixture of two small-molecule solvents, a and b, having equal molal volumes and having a cohesion energy between an a and a b molecule equal to the average of that between two a molecules

and that between two b molecules, the following relation can be deduced:

$$\ln V_2 = \frac{V_2}{V_1}(A - BV_a') \tag{23}$$

where

$$A = V_1 - \frac{f_2}{RT} - \mu_b V_1^2 \tag{24}$$

and

$$B = (\mu_a - \mu_b)V_1^2 \tag{25}$$

V_a' is the volume fraction of component a in the mixture of a and b (without component 2)

$$V_a' = \frac{V_a}{V_a + V_b} = \frac{V_a}{V_1} \tag{26}$$

If the ab, aa, and bb cohesion energy densities are not additive, in the sense assumed in the derivation of equation (23), another term, $CV_a'^2$, must be included within the parenthesis in that equation.

In case the phase in equilibrium with the solution is not pure component 2, but a gel containing, in addition, either a or b or both (not, in general, in the same ratio as in the solution), the situation and the mathematical expressions for it are considerably more complicated. The same principles and fundamental equations which are applicable to the simpler cases should also be applicable to such a system. However, space will not be taken here to discuss the subject further.

It follows from the form of equation (23) that the solubility is very sensitive to the value of the function in parenthesis and so to the composition (V_a') of the solvent mixture, provided μ_a and μ_b are quite different. This is the basis for the well-known fractional precipitation technique for the separation of mixtures of chains of different length. For a given ratio, V_a', the molecules above a certain size tend to precipitate out; those below that size tend to remain in solution.

Equation (23) is similar in form to an empirical equation published by Schulz.[18] The treatment just outlined provides it with a theoretical basis, gives the relationships between the constants involved and other quantities, and indicates the circumstances under which it should be inaccurate and the sort of changes and additions required to make it more generally applicable.

[18] G. V. Schulz, *Z. physik. Chem.*, **A179**, 321 (1937).

After summarizing certain thermodynamic relationships which are applicable to all solutions, approximate equations for the heat of mixing and entropy of mixing have been presented. The second, which leads to Raoult's law if the heat of mixing is zero, has been shown to be very much in error for solutions of long-chain compounds. To replace it, new expressions have recently been derived. These lead to activity equations, containing a single empirical constant, which are in good agreement with a large amount of experimental data.

Starting from these activity equations, such problems as the dependence of osmotic pressure on concentration, the requirements for the separation of a solution into two phases (one being usually a gel), and the solubility of small molecules in gels and of large molecules in low-molecular-weight liquids and liquid mixtures have been dealt with. Certain previously known empirical relations have been given a theoretical basis and have been corrected and extended.

C. DETERMINATION OF MOLECULAR WEIGHT

H. M. Spurlin

There is no longer any point in arguing the reality of the concept of molecular weight as applied to cellulose and its derivatives. The justification for this statement will be found in Chapter II and in Section A of this chapter. In particular, the discussion of polymolecularity in Section D of Chapter II is important from the standpoint of interpreting molecular-weight determinations, that is, whether it is the weight-average or number-average which is significant in a particular case. Also, chemical methods for determining molecular weights have been discussed in Section C of Chapter II. This section, therefore, is devoted primarily to a discussion of physical methods of molecular-weight determination.

As cellulose and its derivatives are not volatile, all satisfactory methods go back to a determination of the thermodynamic properties of solutions. These have been reviewed in Section B of this chapter, where it is shown that both theoretically and experimentally the laws of ideal solutions apply to solution of large molecules if the solutions are sufficiently dilute. This conclusion follows from the laws of statistical mechanics; the case is analogous to that of the behavior of a real gas which approaches that of an ideal gas as the pressure is reduced regardless of the number of internal degrees of freedom of the gas molecule. However, since much doubt has been cast on the validity of this conclusion in the recent literature, reference may be made to two recent papers where an attempt has been made to present the subject clearly in a manner specifically applicable to solutions of large molecules.[1, 2]

As was shown in Sections A and B of this chapter, the laws of ideal solutions hold for high-molecular-weight compounds only at infinite dilution, and the deviations at concentrations accessible to measurement are quite appreciable except in the case of solutions where precipitation is about to occur. The latter solutions are difficult to work with, especially in the case of products which require powerful solvents to put them into

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[1] A. J. Staverman and J. H. van Santen, *Rec. trav. chim.*, **60**, 65 (1941).

[2] J. J. Hermans, *Rec. trav. chim.*, **60**, 370 (1941).

solution initially, because of such factors as the presence of fiber structure and overdrying. It is necessary, therefore, to use methods of sufficient precision to allow accurate measurements in dilute solutions if satisfactory results are to be obtained. Even in this case, the variation of activity with concentration should be determined in order to make sure that deviations from ideality are not important in the range accessible to measurement. Except in the case of the ultracentrifuge, the accuracy of measurement in that range where the laws of ideal solutions hold is not sufficient for most purposes, and it is preferable to work in more concentrated solutions and to extrapolate to infinite dilutions. Methods for carrying out this extrapolation will be discussed later.

1. Cryoscopic and Ebullioscopic Methods

The usual method for determining the molecular weights of organic substances is to measure the depression of freezing point or the elevation of boiling point of a solution in an appropriate solvent. Much mystification was introduced into cellulose chemistry by attempts to apply these methods. Their failure was due to the necessity for working in concentrated solutions in order to secure measurable effects. As is pointed out in Section B of this chapter, and as is further evident from Figure 21,[3] the activity of the solvent is substantially independent of the molecular weight of the cellulose derivative for concentrations above 10%. At concentrations of 1 to 2%, which are the highest desirable if an accurate extrapolation to zero concentration is to be carried out, the lowering of the freezing point of solvents with the most favorable molar freezing-point constants (64° lowering for a molar solution in camphenilone[4]) would be about 0.007 to 0.02° for a molecular weight of 100,000. This is barely within the range of the most careful experimental technique, and it is to be hoped that future investigators will re-examine the freezing-point method with the object of covering the range below a molecular weight of 30,000, which is difficult to cover with osmotic-pressure methods because of diffusion of the solute through the membrane. It must not be forgotten, however, that, as was shown by Freudenberg,[5] the freezing-point method is very susceptible to error in the case of cellulose derivatives because of their tendency to cause delayed crystallization and because of the probable presence of small amounts of low-molecular-weight impurities.

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[3] G. V. Schulz, *Z. physik. Chem.*, **A184**, 1 (1939).
[4] J. Pirsch, *Ber.*, **66B**, 1694 (1933).
[5] K. Freudenberg, *Naturwissenschaften*, **17**, 959 (1929).

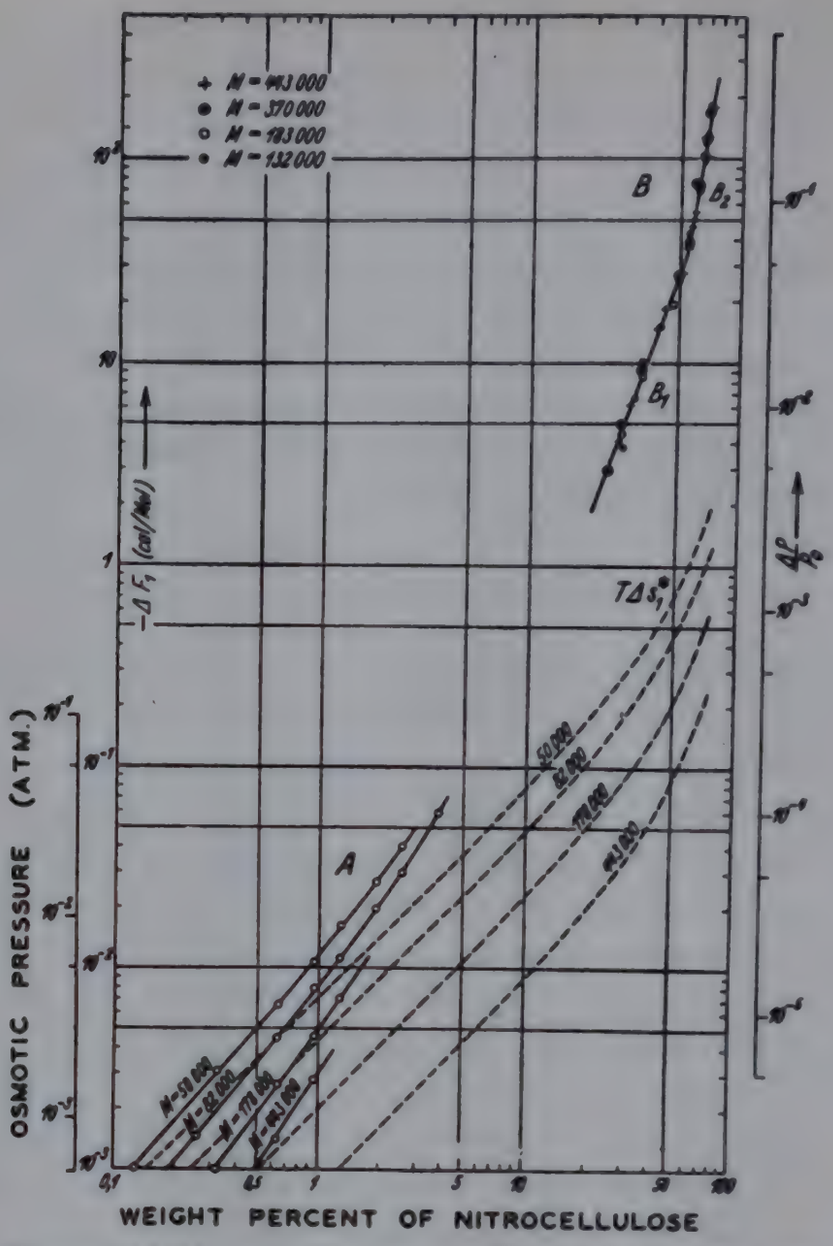

FIG. 21.—FREE ENERGY (ΔF_1) OF THE SOLVENT IN NITROCELLULOSE-ACETONE SOLUTIONS OF VARIOUS CONCENTRATIONS (SCHULZ[3]).

A—From osmotic pressures.

B—From vapor pressures.

$T\Delta s_1^*$—Calculated portion of the free energy arising from the entropy of mixing (broken lines).

Osmotic pressures and vapor-pressure lowerings are indicated by the auxiliary ordinate scales.

2. Osmotic-Pressure Method

It was recognized quite early that solutions of colloids, including cellulose derivatives, gave easily measured osmotic pressures. It was not until Wo. Ostwald[6] pointed out the necessity of extrapolating to zero concentra-

[6] Wo. Ostwald, *Kolloid-Z.*, **23**, 68 (1918); **49**, 60 (1929).

tion that satisfactory molecular-weight determinations could be carried out by osmotic or any other physical methods. This observation was immediately followed by a series of investigations in many laboratories, with the result that within a few years all of the important cellulose derivatives had been sufficiently well characterized to allow correlation of

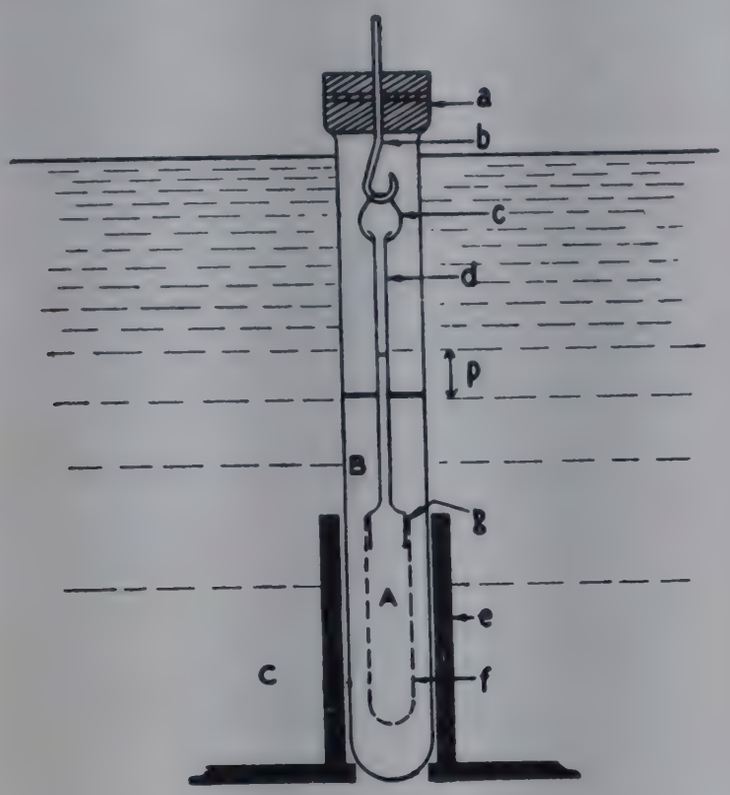

FIG. 22.—DOBRY OSMOMETER (DOBRY[8]).

A—Solution.
B—Solvent.
C—Thermostat water.
a—Stopper.
b—Glass hook.
c—Platinum wire.
d—Capillary.
e—Support.
f—Semipermeable membrane.
g—Cylindrical tube on which membrane is attached.
p—Difference in liquid levels due to osmosis.

the molecular weight with viscosity, end-group content, and physical properties of films and filaments.

The most long-continued series of investigations on osmotic pressures of solutions of cellulose derivatives was initiated by J. Duclaux[7] and continued by his coworkers, particularly Dobry. Dobry[8, 9, 9a] is responsible for the first conclusive experimental demonstration that the molecular weight is independent of the solvent employed and that the results of

[7] J. Duclaux and E. Wollman, *Compt. rend.*, **152**, 1580 (1911).
[8] A. Dobry, *J. chim. phys.*, **32**, 46 (1935).
[9] A. Dobry, *Bull. soc. chim.*, [5], **2**, 1882 (1935).
[9a] A. Dobry, *J. chim. phys.*, **32**, 50 (1935).

osmotic-pressure measurements are incompatible with the micellar theory of solutions as enunciated around 1935.

The methods employed in the Duclaux laboratory are characterized by their simplicity.[8, 9] Sacs of denitrated collodion, fastened to tubes in

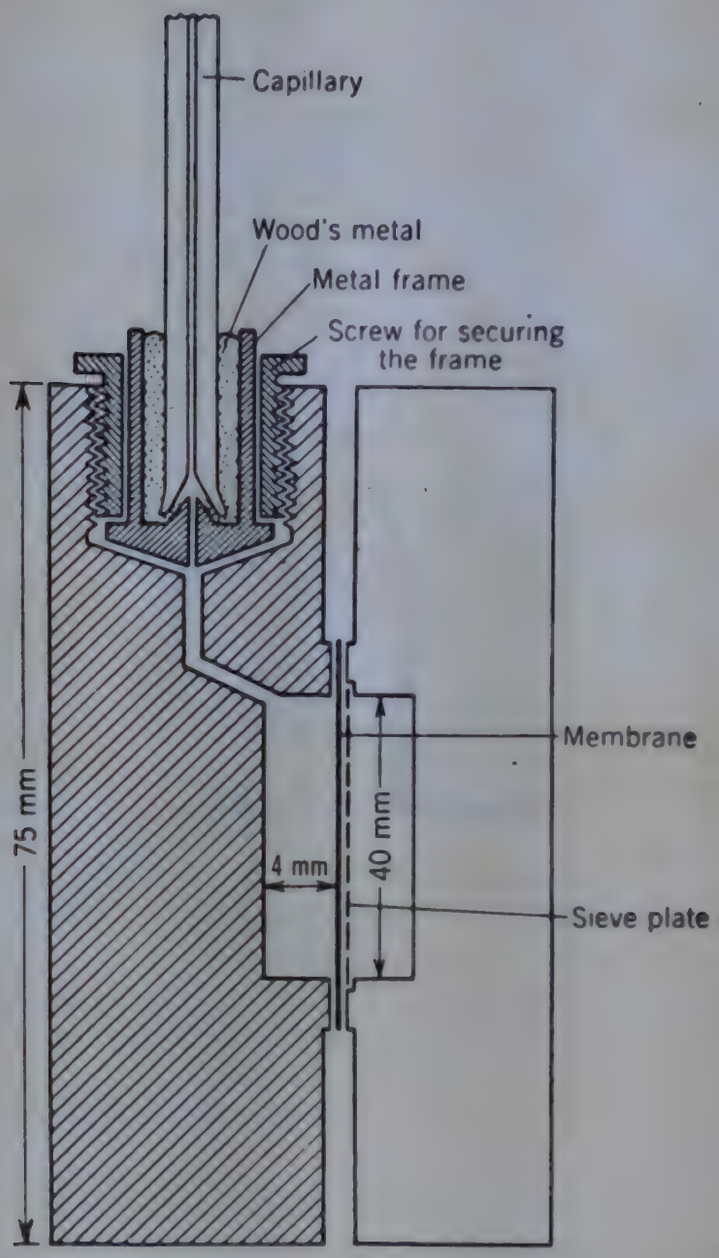

FIG. 23.—HERZOG AND SPURLIN OSMOMETER AS MODIFIED BY MEYER: CROSS SECTION (MEYER[10]).

which the osmotic pressure can be measured, are filled with solution; the sacs are then immersed in pure solvent until equilibrium is reached (Fig. 22). Advantages of the method are its cheapness and the fact that, due to the

[10] K. H. Meyer, *High Polymers*, Vol. IV, *Natural and Synthetic High Polymers*. Interscience, New York, 1942, pp. 13–14.

relatively long time required for a determination as well as the large area of the membrane, low-molecular-weight impurities have ample opportunity to come to equilibrium on both sides of the membrane. One disadvantage is the elasticity of the membrane, which allows expansion as the osmotic pressure rises and necessitates both a relatively long time for equilibrium to be reached and analysis of the solution after the measurement. It is also difficult to secure compensation for changes of temperature without the use of ground-glass joints, which introduces the problem of obtaining sealing media inert to organic solvents. The method merits

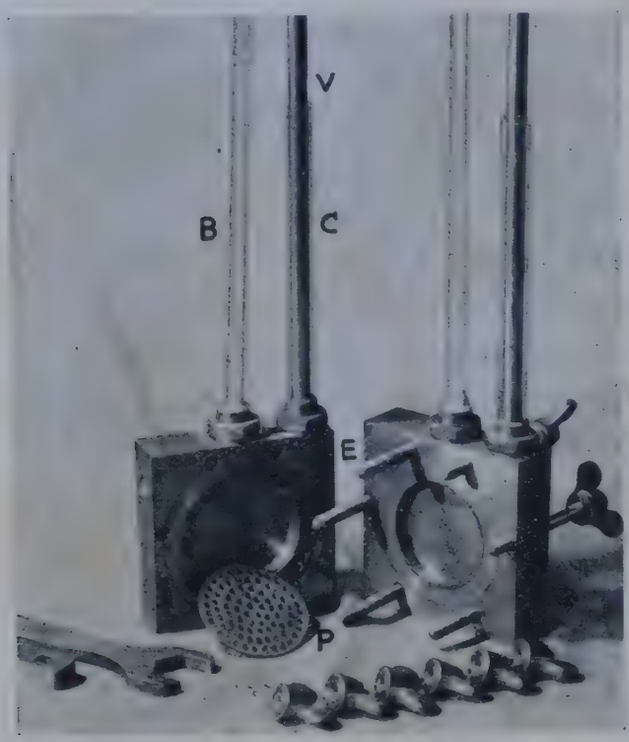

FIG. 24.—HERZOG AND SPURLIN OSMOMETER AS MODIFIED BY MEYER (MEYER[10]).

B—Capillary tube. E—Metal body.
C—Filling tube. P—Perforated plate.
V—Valve.

more widespread consideration; according to private communications, the chief difficulty experienced in this country has been the preparation of sacs with satisfactory permeability.

A somewhat different outlook was behind the development of the cell of Herzog and Spurlin,[11] a slight modification (Figs. 23 and 24) of which has been used by K. H. Meyer and his coworkers[12] in their numerous re-

[11] R. O. Herzog and H. M. Spurlin, *Z. physik. Chem.*, Bodenstein-Festband, p. 239 (1931).

[12] C. G. Boissonnas and K. H. Meyer, *Helv. Chim. Acta*, **20**, 783 (1937).

searches on polymers. Here the objectives were to secure rapid attainment of equilibrium; to avoid errors due to minor changes of temperature; to confine the membrane and to use a fine capillary for the observation of the osmotic-pressure rise, so that the volume of the solution would not change during measurement and analysis of the solution after completion of the run would be unnecessary; to use the very satisfactory, commercially available, flat membranes; and to avoid entirely the use of any cement or sealing agent which might dissolve and falsify the readings. These objectives were obtained by clamping the membrane between two metal blocks, held together by means of several strong bolts. Cavities of equal volume on each side of the membrane communicated with capillary tubes of equal diameter, so that a rise in one side would be balanced by a fall in the other, making the attainment of equilibrium twice as rapid as in the case when the solvent side has a large exposed surface. A change of temperature caused an equal rise in height on both sides and, therefore, did not disturb the equilibrium. It was found experimentally that the difference between the surface tension of solution and of solvent was always negligible, thus making a correction unnecessary. Metal needle valves allowed filling and emptying without contamination from grease. Perforated plates supported the membrane, assuring that the volume on the solution side would not change. It is better to use perforated plates on both sides of the membrane, with the holes matching; the device of Montonna[13] (Fig. 25),

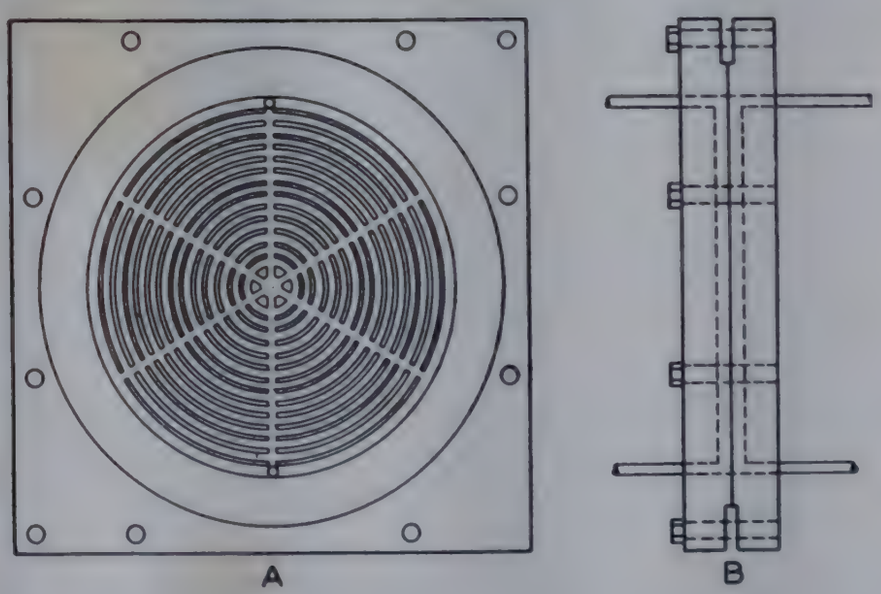

FIG. 25.—MONTONNA OSMOMETER (MONTONNA AND JILK[13]).

A—Front view showing arrangement of ridges and grooves. B—Cross section.

[13] R. E. Montonna and L. T. Jilk, *J. Phys. Chem.*, **45**, 1374 (1941).

n which the membrane is supported on both sides on a metal block in which intercommunicating annular grooves have been turned, appears to have advantages over the perforated plates.

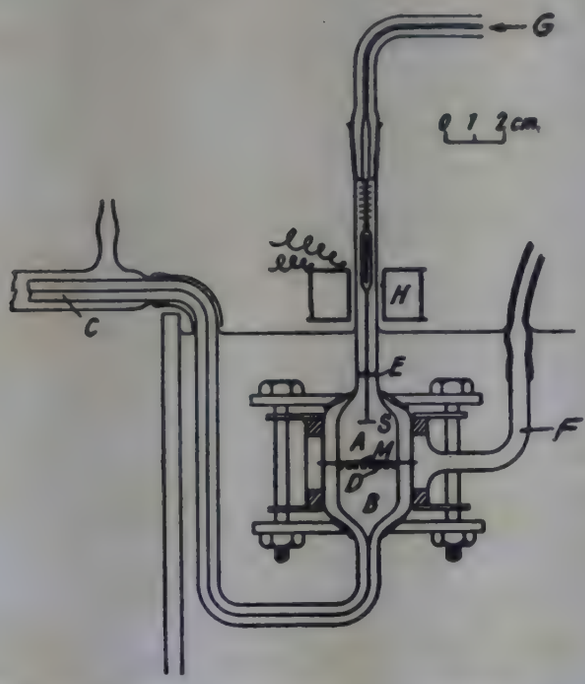

FIG. 26.—CARTER AND RECORD COUNTERPRESSURE OSMOMETER (CARTER AND RECORD[14]).

A—Chamber for solution.
B—Chamber for solvent.
C—Capillary for observing solvent meniscus position.
D—Perforated brass membrane support.
E—Etched mark for solution level.
F—Mercury seal.
G—Inlet for counterpressure.
H—Magnetic stirrer.
M—Membrane.
S—Platinum disk for stirring.

With this apparatus, measurement of osmotic pressure can be made in a few hours if the pressure is initially adjusted to almost the correct value or if the method of compensation is used; if the latter method is used, the rate of flow against the pressure is plotted, and the pressure corresponding to zero rate of flow is found by interpolation. It should be noted that the method of compensation is unsuitable if mixed solvents are used or the sample contains diffusible impurities, particularly electrolytes. One of the initial difficulties with this apparatus, that is, sealing the glass tubes into the metal body, seems to have been overcome by the use of fusible metal.[15] It is fortunate that the now unavailable imported membranes can be satisfactorily replaced by suitably swollen cellophane.[14, 16]

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[14] S. R. Carter and B. R. Record, *J. Chem. Soc.*, **1939**, 660.

[15] W. Herz, Dissertation, Univ. of Berlin, 1934; *Cellulosechem.*, **15**, 95 (1935). See also ref. 12, p. 915.

[16] T. Alfrey, A. Bartovics, and H. Mark, Buffalo meeting, Am. Chem. Soc., Sept. 7–12. 1942.

A further development of osmometers was undertaken by Carter and Record.[14] By sacrificing the advantages of equal volume and equal capillaries on each side of the membrane, they were able to introduce mechanical stirring of the solution, which undoubtedly is advantageous (Fig. 26). As an all-glass apparatus was used, the difficulties of sealing-in the capillaries were avoided. It was found possible to prevent leakage around the edges of the membrane by using a mercury seal. Very close temperature control and correction for surface tension are necessary with their instrument. In considering the advantages for stirring in the osmometer, it should be remembered that if the membrane is horizontal, as in the case of the Carter-Record and Schulz instruments, convection cannot facilitate mixing as easily as when the membrane is vertical.

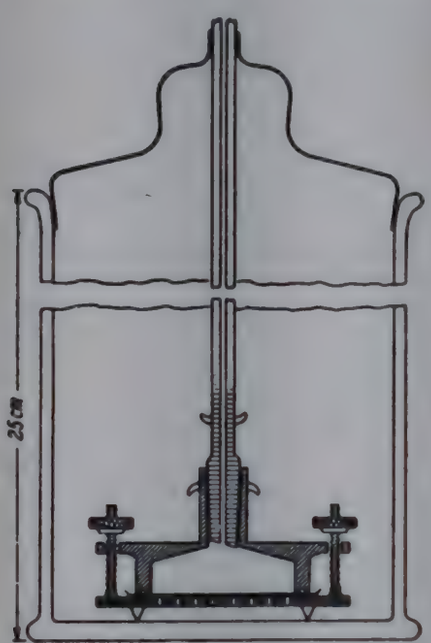

FIG. 27.—SCHULZ OSMOMETER (SCHULZ[17]).

Probably more than half of the osmotic-pressure measurements on cellulose derivatives so far reported have been obtained in the apparatus of Schulz[17] (Fig. 27). This apparatus consists of a metal vessel containing the solution and provided with a capillary. Over the open face of the metal container a membrane supported by a perforated plate is clamped. The assembled unit filled with solution is plunged into solvent. This apparatus appears to have no advantages over any of those just described. It is essentially the simplest apparatus of Dobry adapted to flat membranes. The ground-glass joint in contact with the solution is very undesirable, but this could be avoided by the use of a metal-to-glass seal.

One of those controversies which makes cellulose chemistry so interesting to follow has been on the next method to be discussed, that of isothermal distillation. As applied by Ulmann, working in Hess's laboratory, this method,[18] based on a modified Frazer-Patrick technique[19] and involving the determination of the negative pressure (or pull) that must be applied to a column of liquid supported by capillary attraction in a porous plate,

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[17] G. V. Schulz, *Z. physik. Chem.*, **A176**, 317 (1936).

[18] M. Ulmann, *Z. physik. Chem.*, **A156**, 419 (1931); **A164**, 312 (1933).

[19] J. W. C. Frazer in *Colloid Symposium Annual*. Vol. VII, John Wiley, New York, 1930, p. 259.

seemed to lead to values of molecular weights of cellulose derivatives indicating dissociation almost to the monomer stage in dilute solution. These results, of course, threw doubt on the viewpoints as to the molecular weight of cellulose accepted in this book. Hess and Surányi,[20] in a study of the sources of error inherent in Ulmann's technique, have shown, however, that the uncertainty of the results is in the neighborhood of 1 to 2 mm. of Hg. As this is the order of magnitude of the pressures in the region where Ulmann claimed to have demonstrated dissociation, it appears justified to dismiss as unfounded the supposition of dissociation of cellulose derivatives in dilute solution.

3. Extrapolation of Molecular-Weight Data to Infinite Dilution

As has been pointed out, accurate values of molecular weight determined by osmotic-pressure, cryoscopic, or other methods, the sensitivity of which is such that measurements in extremely dilute solutions are not sufficiently precise, depend upon an extrapolation to infinite dilution from the region where reasonably precise determinations can be carried out (0.5 to 2% solutions). As in all methods of extrapolation, assurance as to the theoretical course of the curve is of great help. Unfortunately, complications occur in some cases, and these have served to confuse the issue.

The almost universally used method of treating osmotic-pressure data is to plot the osmotic pressure (P) divided by the concentration (C) against the concentration, as is shown in Figure 28.[21] It is evident from these curves that the theoretical requirement (Section B of this chapter) that the lines should be straight and parallel to one another in the low-concentration range is well fulfilled in these particular cases. However, other workers have obtained curves on plotting P/C against C. Sometimes the curves are concave upward as in Figure 29,[11] at other times concave downward, as in Figure 30.[9a] It is tempting to ascribe these effects to experimental error, especially as the curvature is most noticeable in the low-concentration range, where the measurements are most inaccurate. However, two of the most prolific workers in this field, Dobry and Schulz, claim that the curvature, though not always prominent, is real. Also, Steurer[21a] has shown that in pure hydrocarbon solvents three or four molecules of ethylcellulose are very strongly associated. Below 0.1% concentration, the P/C versus C curves tend to bend up. The association

[20] K. Hess and L. A. Surányi, *Z. physik. Chem.*, **A184,** 321 (1939).

[21] H. Mark, *High Polymers*, Vol. II, *Physical Chemistry of High Polymeric Systems*. Interscience, New York, 1940, p. 241, Fig. 78.

[21a] E. Steurer, *Z. physik. Chem.*, **A190,** 1, 16 (1941).

is completely eliminated by addition of small amounts of polar solvents, normal straight lines then being found. As the abnormality in this case is definitely due to association, the question of extrapolation will be reviewed and a cause of curvature due to association will be suggested.

An attempt to systematize this behavior has been made by Schulz,[22] who based his deductions on the fact that the osmotic pressure is independ-

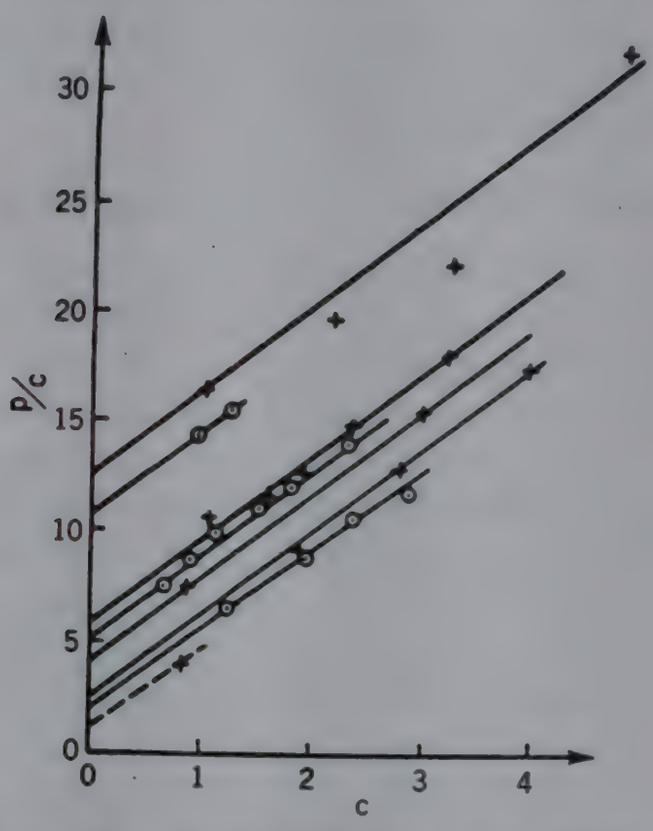

FIG. 28.—OSMOTIC PRESSURE DATA WHICH SHOW THE NORMAL BEHAVIOR (MARK[21]).

The data plotted are for nitrocelluloses of molecular weights from 20,000 to 100,000 dissolved in acetone.

ent of molecular weight in the region above 10% concentration (Fig. 21). It is logical to make the further assumption, as was done by Wo. Ostwald,[6] that the contribution to osmotic pressure which is independent of molecular weight is also a factor at low concentrations, and is not negligible in comparison to the van't Hoff osmotic pressure. Ostwald, in applying the necessary correction, made use of the relationship

$$P = \frac{C}{M} RT + kC^n \qquad (1)$$

[22] G. V. Schulz, *Z. physik. Chem.*, **A180**, 1 (1937); see also ref. 3, p. 911.

finding experimentally that n was usually nearly 2 and, therefore, that P/C was nearly linear with C. This assumption harmonizes with the development in Section B of this chapter, according to which the deviations from the laws of ideal solutions are a function of the concentration. Schulz, however, seemed to secure better agreement with his experimental data if the additional term was an exponential function of P:

$$\frac{P}{C} = \frac{RT}{M} + P\left(\frac{k}{P}\right)^{\frac{1}{\nu}} \qquad (2)$$

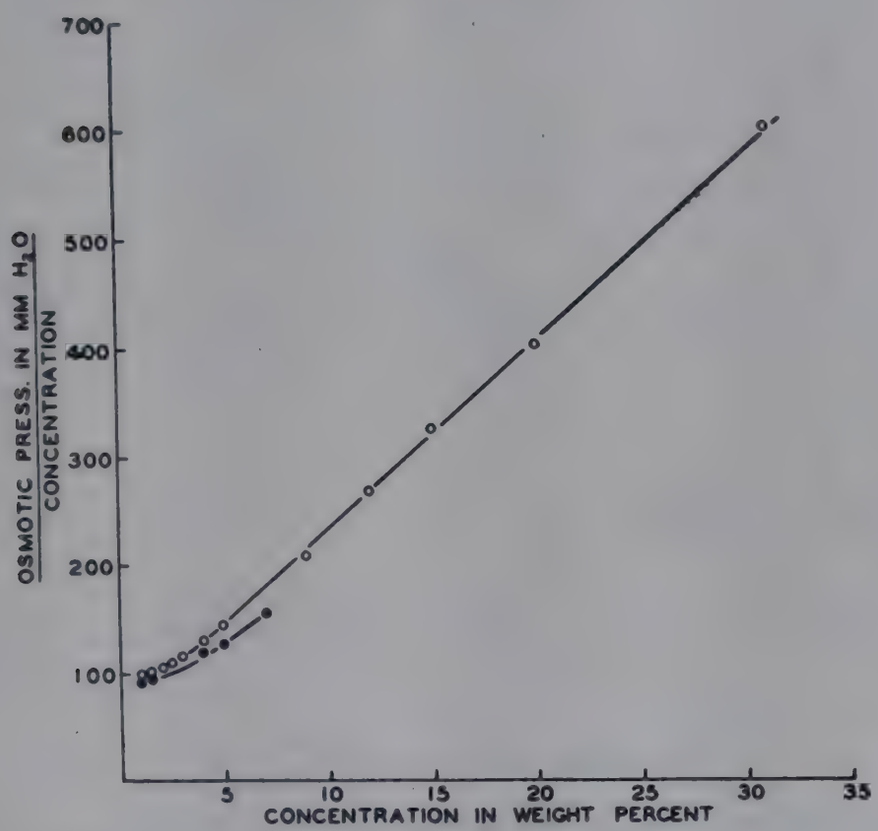

FIG. 29.—DEVIATION FROM LINEAR BEHAVIOR SHOWN BY P/C VERSUS C CURVES FOR SOLUTIONS OF BENZYLCELLULOSE IN METHYL CELLOSOLVE ACETATE (2-METHOXYETHANOL ACETATE) (HERZOG AND SPURLIN[11]).

According to this equation, the course of the P/C versus C curve would become very abnormal for low values of M, and correspondingly high values of P. Also, the $P/C - C$ curve would have to have infinite slope at zero concentration. Both of these types of behavior are without precedent. It appears that the Schulz equation does not have adequate theoretical background.

A clue to possible reasons for the observed behavior is found by examination of Figure 17 of Section B (p. 903). It is seen that, in cases of high

specific interaction between chains, very complex activity-concentration curves are obtained. If it is further assumed that a given sample contains molecules of widely differing molecular weight and specific interaction, almost any shape of P/C against C curve could be realized.

The chief difficulty in using this concept is that acetone, which is a very good solvent for nitrocellulose and, therefore, presumably possesses a low interaction term, has been claimed by both Dobry and Schulz to give a curved relationship.

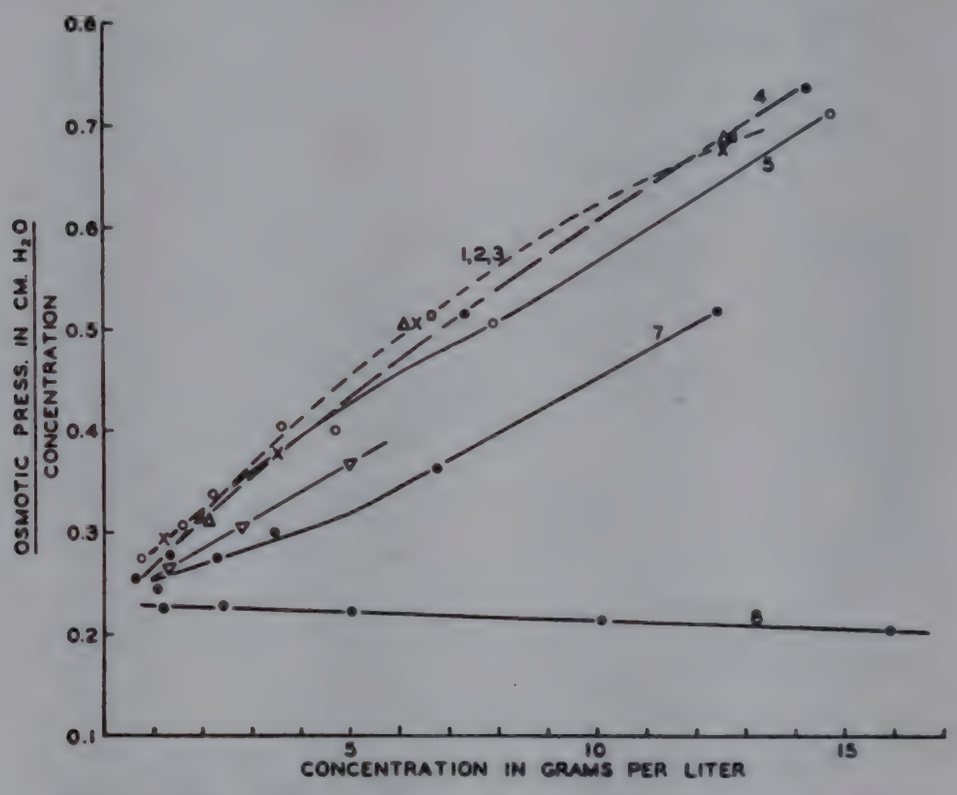

FIG. 30.—DEVIATION FROM LINEAR BEHAVIOR SHOWN BY P/C VERSUS C CURVES FOR SOLUTIONS OF NITROCELLULOSE IN VARIOUS SOLVENTS (DOBRY[9a]).

1—Ethyl benzoate + 11% ethanol.
2—Methyl salicylate + 20% methanol.
3—Acetophenone + 3% ethanol.
4—Cyclohexanone + 5.8% ethanol.
5—Acetone.
6—Acetic acid.
7—Methanol.
8—Nitrobenzene.

It is not necessary to abandon the idea of interaction between chains as the cause of the observed facts, however. As was shown in Section A of this chapter, there is considerable evidence that many samples of cellulose derivatives contain along the chains localized spots, possibly metallic salts or regions of low substitution, which have a pronounced tendency to adhere to one another, especially in solvents containing no hydroxyl groups. As the concentration is raised, these spots will have a greater tendency to associate with one another, increasing the molecular weight

and tending to decrease the osmotic pressure. On the other hand, as it may be assumed that most of the molecule is perfectly normal, there will be an increase in osmotic pressure with concentration due to the effects discussed in Section B of this chapter, which are independent of molecular weight and are due to entropy of curling of the molecule. In cases where good solvents such as acetone are used, the entropy of curling may be assumed to lead to an essentially linear relationship between P/C and C in the low-concentration range. Any curvature must be ascribed to the association effect or some other abnormality peculiar to the solvent or particular sample used.

Quantitative treatment of this effect is very easy in the case where, at most, one point of association per molecule exists. As in all cases of association, the molar concentration of a dimer will be a constant times the concentration of the monomer squared. If the number of moles per liter of unassociated molecules is taken equal to x, then, for this case of one active spot per molecule, the dimer will be kx^2. Thus the actual number, N, of moles per liter will be

$$N = x + kx^2 \tag{3}$$

while the concentration, C, of the monomer in moles per liter will be

$$C = x + 2kx^2 \tag{4}$$

The portion of the osmotic pressure due to the number of dissolved molecules will be reduced, because of association, by the factor N/C.

$$\frac{N}{C} = \frac{1 + kx}{1 + 2kx} = \frac{3 + \sqrt{1 + 8kC}}{2 + 2\sqrt{1 + 8kC}} \tag{5}$$

By differentiation

$$\left[\frac{d^2\left(\frac{N}{C}\right)}{dC^2}\right]_{C \to 0} = 8k^2 \tag{6}$$

The positive second derivative indicates that the P/C versus C curve will be concave upward, that is, similar to the curve for f = 1 (Curve 5) in Figure 31.

The treatment of cases where more than one spot of possible association per cellulose chain exists is rendered more complex because internal association with ring formation is possible. This cannot be neglected, as this tendency is not a function of concentration, and will be a predominating influence at low concentrations where association between different molecules is slight. The treatment in this case will differ from that presented

for the case of a single active spot (equations (3) to (6)) in that, in addition to the dimer, the trimer, tetramer, and so on, will all be present. The total number of moles of solute may be expressed as a power series in x, the number of moles of monomer. In this series, the term in x^2 will represent the concentration of dimer, that in x^3 the trimer, and so forth. The

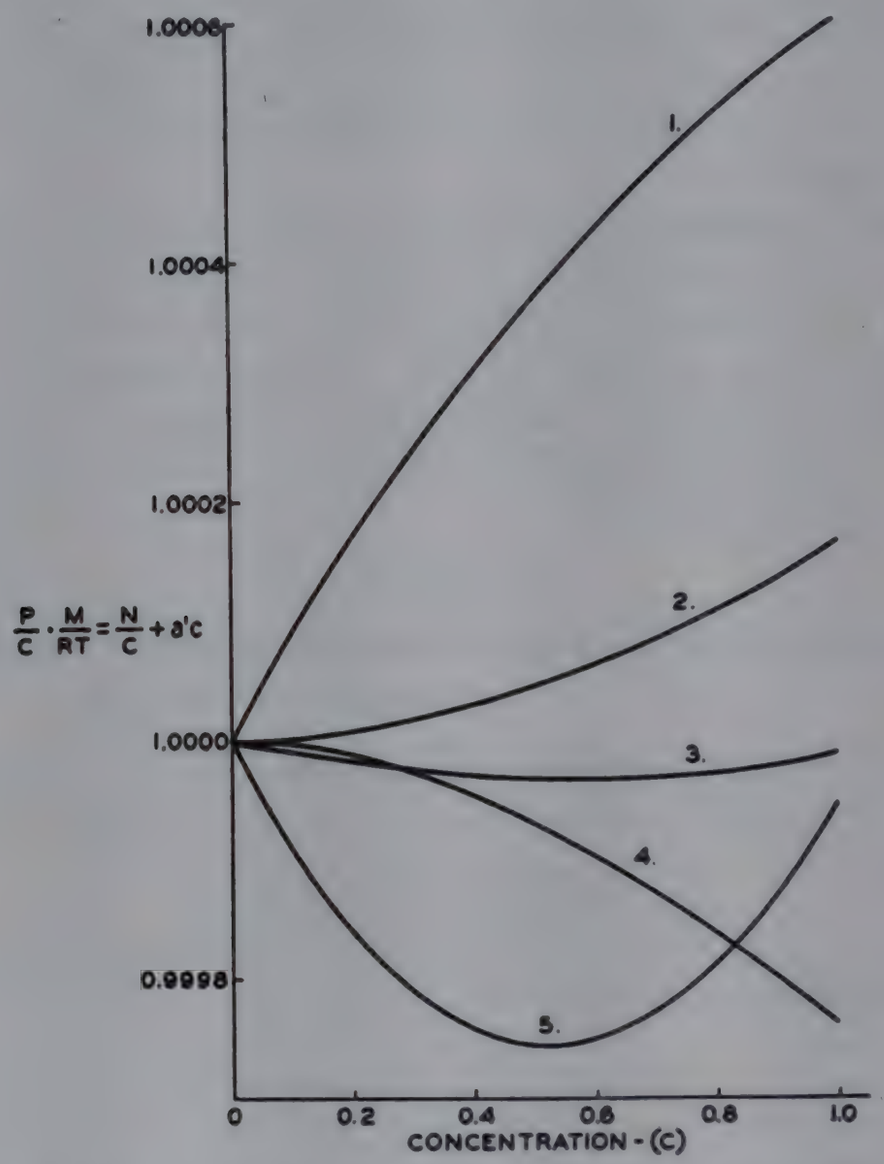

FIG. 31.—CALCULATED CURVES SHOWING EFFECT OF ASSOCIATION ON OSMOTIC PRESSURE.

Curves: 1. f (functionality) = 4, $k_1 = 1$, $k_2 = 1$; 2. f = 2, $k_1 = 0.063$, $k_2 = 0.3$; 3. f = 3, $k_1 = 0.5$, $k_2 = 1$; 4. f = 2, $k_1 = 0.25$, $k_2 = 1$; 5. f = 1, $k_1 = 0.016$. The units of concentration (C) depend only upon the units chosen for k_1.

corresponding series for the concentration of monomer (including that present in the associated form) will be obtained by multiplying the x^2 term by 2, the x^3 term by 3, and so forth. The number of molecules containing rings due to internal association will be, in each case, a constant times the

number of units without rings and may be combined with the association constants so that equations (3) to (5) will now read:

$$N = x + ax^2 + bx^3 + \ldots\ldots \tag{7}$$

$$C = x + 2ax^2 + 3bx^3 + \ldots\ldots \tag{8}$$

and

$$\frac{N}{C} = \frac{1 + ax + bx^2 + \ldots\ldots}{1 + 2ax + 3bx^2 + \ldots\ldots} \tag{9}$$

At zero concentration, it may be shown that this function has a negative rate of change of slope when plotted against C only if the constant b is greater than $2a^2$. It may further be proved that, regardless of the functionality of the associating molecules (number of active association points per molecule), it is impossible to have a negative second derivative if association uncomplicated by internal ring formation is the only phenomenon occurring. If, however, there are enough potential spots of association per monomer molecule, the possibility of ring formation increases enormously as the molecules associate, due to the increasing functionality.

In order to allow visualization of the manner in which ring formation influences the shape of the P/C versus C curves, calculations have been carried out for all functionalities of the monomer up through four. The following procedure was adopted: the concentration of dimers, trimers, etc., was calculated by the method of Flory[23] using the assumption that the reactivity of a given potential bonding point was independent of the state of reaction of the rest of the molecule. This calculation so far does not take into account ring formation between bonds in an individual molecule or an association of molecules. The chance of any two spots to undergo ring formation in an individual molecule was assumed to be proportional to the square of the concentration of potential bonds in the molecule and independent of the concentration of the molecules in the solution. This is, admittedly, a doubtful assumption but should be conservative. The number of molecules with single rings was then determined by multiplying the chance of formation of an individual kind of ring by the number of kinds of rings. In a similar fashion, the number of molecules with two rings was calculated from the number with one, and so on. It was found that, with two potential bonding points per cellulose chain, high values of the constant determining ring formation led to a curve of P/C against C which was slightly convex upward. The effect is small, however. With

[23] P. J. Flory, *J. Am. Chem. Soc.*, **63**, 3083, 3091, 3096 (1941).

three potential bonding points per chain, no combination of association and ring-formation constants can lead to such negative curvature. With four or more potential cross-linking bonds per cellulose chain, the possibility of ring formation is so greatly increased as the degree of association rises that there is a marked preference of formation of trimer from dimer, and a negative second derivative P/C with respect to C results from all but small values of the ring-formation constant. Curves showing P/C against C are shown in Figure 31. In the caption are given the values assumed for the constants k_1 (the bimolecular association of a bond in one molecule with one in another molecule) and for k_2 (the ring formation reaction).

If this explanation of the occasionally observed curvature of the reduced osmotic-pressure curve is the correct one, the uncertainty of extrapolation is much reduced; it will be noted for all of the cases treated in Figure 31 that the curvature becomes less as the concentration approaches zero. This behavior contrasts with that required by the extrapolation equation of Schulz (equation (2)), which demands that the curvature increase without limit as the concentration approaches zero. It is recommended, therefore, that extrapolations always be carried out in such a manner that the curvature becomes slight at zero concentration.

A further consequence of this treatment is that solvents should be chosen which reduce the association to a minimum. A good test of this will be to examine the viscosity-concentration curves (see Section A of this chapter), choosing that solvent which gives the lowest relative viscosity in concentrated solutions. Usually hydroxyl-containing solvents will be best from this standpoint. There is no objection to the use of mixed solvents unless the compensation method is used.

Another factor which could influence the course of the reduced osmotic-pressure curves is the preferential association of one component of a mixed solvent with the derivative. A quantitative treatment of this effect has not been attempted, but it should be noted that some of the cases examined by Dobry involved mixed solvents.

4. The Ultracentrifuge Method

At present, the method for determining molecular weights of high-molecular-weight substances which has won most widespread acceptance depends on the determination of the sedimentation equilibrium of a very dilute solution in the ultracentrifuge. The particular value of the ultracentrifuge is that, by using it, weight-average molecular weights may be

determined directly, without the necessity of a tedious fractionation process.

As an excellent discussion of the application of the ultracentrifuge exists,[24] no attempt will be made to review the subject here. It should be remembered that the best basis at present for correlating viscosity with molecular weight in the case of cellulose and its derivatives is the work of Kraemer and his associates using the ultracentrifuge.[25]

5. Molecular Weight and Viscosity

Much of the early work on correlating molecular weights of cellulose derivatives with their other properties depended on the application of Staudinger's rule, which states that the specific viscosity, η_{sp}, of a very dilute solution is proportional to the molecular weight.[26]

$$\eta_{sp} = \eta_{rel} - 1 = \frac{\eta_{\text{solution}}}{\eta_{\text{solvent}}} - 1 = K_{\text{m}} \cdot M \cdot C \qquad (10)$$

This rule was founded mainly on cryoscopic and end-group determinations with very low-molecular-weight polymers. The uncertainty in extrapolating these results to high-molecular-weight polymers caused the method to be received with much doubt. As reliable molecular-weight determinations by the ultracentrifuge and osmotic-pressure techniques have become available,[24] it has become evident that the molecular weights of fractionated cellulose derivatives do determine their viscosities in a given solvent. The linear relationship of Staudinger is often useful over limited ranges of molecular weight, but not always applicable. It is to be hoped that future investigators will search for solvents giving a close approximation to Staudinger's law with the important cellulose derivatives.

The theoretical basis of the viscosity rule is discussed in Section E of this chapter, and practical points in Section F. The necessity for measuring viscosity in extremely dilute solution in order to avoid error has been stressed by Staudinger but needs to be re-emphasized. As is the case with osmotic pressure, extrapolation to infinite dilution is the only satis-

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[24] T. Svedberg and K. O. Pedersen, *The Ultracentrifuge*. Clarendon Press, Oxford, 1940.

[25] E. O. Kraemer and J. B. Nichols, in T. Svedberg and K. O. Pedersen, *The Ultracentrifuge*, pp. 418–421; R. Signer, in T. Svedberg and K. O. Pedersen, *The Ultracentrifuge*, pp. 436–439; see ref. 24, above.

[26] H. Staudinger, *Die hochmolekularen organischen Verbindungen*. J. Springer, Berlin, 1932.

factory method. This may be done graphically by plotting η_{sp}/C against C, or by using one of the numerous viscosity-concentration equations described in Section F.

Numerous workers in the field have pointed out the possibility of determining molecular weights directly from a single viscosity measurement carried out at high concentration, especially if a universal concentration-viscosity relationship occurs. However, the effects of association discussed

TABLE 1

VISCOSITY CONSTANTS FOR CELLULOSE AND ITS DERIVATIVES

Substances	Solvent	$K\left(=\frac{\text{D.P.}}{[\eta]}\right)$	Method of measuring D.P.
Cellulose	A.C.S. cupram-monium	260	Ultracentrifuge (equilibrium)[24]
Cellulose acetate[a]	Acetone	230	Ultracentrifuge (equilibrium)[24]
Nitrocellulose[b]	Acetone	270	Ultracentrifuge (equilibrium)[24]
Ethylcellulose	Dioxane	300	Ultracentrifuge (equilibrium)[24]
Methylcellulose[c]	Water	90	Ultracentrifuge (equilibrium)[27]
Butylcellulose[d]	Chloroform	95	Osmotic pressure[28]
Benzylcellulose[e]	Chloroform	85	Osmotic pressure[28]
	m-Cresol	95	Osmotic pressure[28]

[a] 2.38 Acetate groups per glucose residue.
[b] 12.0 ± 0.1% N.
[c] 22.6–31.7% Methoxyl content.
[d] 2.2 Butyl groups per glucose residue.
[e] 2.1–2.2 Benzyl groups per glucose residue.

under the topic of osmotic pressure and in Section A of this chapter are difficult to predict in individual cases. If association occurs, it influences the viscosity to an enormously greater extent at high concentrations than at low. The only safe practice is actually to make measurements at a low concentration.

Constants for determining molecular weights from viscosity data for a number of cellulose derivatives are given in Table 1. These values are included for convenience only and should be used with caution. This is particularly true for the constants which were determined with the aid of osmotic-pressure measurements, as such methods yield a number-average D.P. while viscosity varies nearly as the weight-average. Values

[27] R. Signer and J. Liechti, *Helv. Chim. Acta*, **21**, 530 (1938).
[28] H. Staudinger and F. Reinecke, *Ber.*, **71B**, 2521 (1938).

obtained with the help of the ultracentrifuge are free from this source of error. In this table, Kraemer's form of the relationship

$$\text{D.P.} = K[\eta] \tag{11}$$

is used. D.P. is the degree of polymerization, and $[\eta]$ is the limit of η_{sp}/C as C approaches zero. All of these constants are based on the use of C as grams of solute per 100 cc. of solution.

The intrinsic viscosity, $[\eta]$, is the most convenient property related to molecular weight to determine experimentally. However, unless Staudinger's law is followed, the $[\eta]$ of an unfractionated sample is not related to either the number- or weight-average molecular weight, but to a type of average intermediate between them in the case of most cellulose derivatives. Also, it is unfortunately true that up to the present the relation between $[\eta]$ and molecular weight has not been determined for cellulose or any of its derivatives with sufficient precision to permit the calculation of accurate molecular weights from viscosity data.

One of the disturbing factors in cellulose literature has been the reporting of molecular weights without indicating the value of the constant used or even whether number-average or weight-average molecular weight is meant. As methods for measuring molecular weights have improved, and especially as it has been recognized that viscosity varies nearly as weight-average molecular weight while most of the absolute methods give number-average values, new values of the constants have been published. In view of this uncertainty, it would be quite worth while if every published report would give the intrinsic viscosity, which is a fundamental constant of a material, in addition to the molecular weight calculated by means of the investigator's favorite constant.

In spite of the uncertainty in the exact relationship between molecular weight and viscosity and the fact that the type of molecular-weight average obtained by viscosity measurement does not always correlate as well as the number-average molecular weight with physical properties, the viscosity method will always be the most useful means for following the molecular weight of cellulose derivatives in ordinary practice. The method is now well-established both theoretically and experimentally and only changes in the constants which are immaterial from the standpoint of commercial practice need be anticipated.

D. INFLUENCE OF POLYMOLECULARITY ON PHYSICAL PROPERTIES

H. M. Spurlin

A complete treatment of the properties of cellulose and its derivatives, as well as most other linear high-molecular-weight substances, requires consideration of the fact that any given sample consists of a mixture of molecules of widely differing chain lengths.[1] The significance of this fact from the chemical standpoint has been discussed in Chapter II, Section D. The possible changes in the interrelationships between physical properties as the degree of polymolecularity is changed must also be considered. Two rough divisions of this problem must be recognized: (1) it is possible that either a very uniform or a very polymolecular product will have properties impossible to realize with the other extreme; and (2) the quantitative relationships between such physical properties as viscosity in solution, physical strength, and flexibility of films may differ as the degree of polymolecularity is changed. As will be pointed out in Section F of this chapter, the flow properties of solutions belong in the first of these categories; long molecules become oriented more or less in the direction of flow at lower velocity gradients than do shorter molecules, so that two products of differing degrees of polymolecularity giving the same apparent viscosity at the same concentration with low rates of flow will give different apparent viscosities at high rates of flow. This phenomenon is of considerable importance in applications of solutions such as spraying, brushing, spinning, and film casting, but no attempt seems to have been made as yet to investigate it separately from other variables. Several cases falling in the second category will be discussed later in this section.

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[1] As pointed out by Staudinger (*Melliand Textilber.*, **20**, 781 (1939)), the expression "polymolecular" is preferable to "polydisperse" as a term to describe systems composed of molecules all having substantially the same chemical composition and mode of linkage but differing in chain length. The expression "degree of polymolecularity" is, then, logically the average degree of departure of the chain length from the mean. For most purposes, the weight-average mean is preferable.

1. Action of Plasticizers

As has been pointed out elsewhere in this book, many solvents are so firmly attached to the cellulose-derivative molecule that the behavior of the resulting products is similar to that of a derivative with very large substituents. In Section A of this chapter, it was shown that, in general, this firm attachment of solvent results in a lessening of forces between the chains; in Section G it will be shown that a loose packing with low forces between chains leads to a flexible, extensible product. Plasticizers are simply high-boiling solvents which are admixed with a high-molecular-weight polymer in order to secure a softer, more flexible product or to facilitate manipulation at high temperatures.

Plasticizers may be roughly grouped into two classes, those which are good solvents and act in the manner just described, and those which are poor solvents. The so-called nonsolvent (really poor-solvent) plasticizers, such as castor oil when used with nitrocellulose, have great technical importance. By their use, very flexible products can be obtained without the production of excessive stickiness on warming and permanent distortion under load. There is no reason to believe in the existence of much solvation in the case of nonsolvent-type plasticizers. As was pointed out by Ott,[2] it seems that, in this case, there exists an interpenetrating network of slightly swollen cellulose-derivative filaments and sheets holding a plasticizer-rich phase by capillary attraction.[3] The two phases are not to be considered as having definite boundaries, but rather as gradually merging into one another, individual cellulose chains occasionally being partially held in the solid framework and partially sticking into the fluid phase. The flexibility of such a system will obviously be determined to a considerable extent by the viscosity of the fluid phase. This, in turn, will depend on the amount of cellulose derivative dissolved in the fluid phase. As was pointed out in Section A, the solubility of a polymer is very strongly dependent on its molecular weight, so that even a relatively poor solvent such as castor oil will dissolve the low-molecular-weight portions of nitrocellulose with a resulting increase in viscosity of the fluid phase and reduction of flexibility, especially at low temperatures.

A certain amount of solvent or swelling action is indispensable if a stable gel is to be obtained. This is shown by the fact that, while small amounts of a true nonsolvent, such as a paraffin oil, may be incorporated in a cellulose derivative, incorporation of enough to secure a really flexible

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[2] E. Ott, *Ind. Eng. Chem.*, **32**, 1641 (1940).

[3] See also O. Kratky, *Kolloid-Z.*, **70**, 14 (1935).

product is only possible if some tendency for solvent action exists. The structure of a material plasticized with a poor solvent may thus be pictured as grading gradually from the high-molecular-weight framework which supports the load, through a gel phase which stabilizes the structure, to the finely dispersed solvent phase containing the very lowest-molecular-weight portions in true solution. It is evident that a certain degree of polymolecularity will promote the formation of this type of structure by ensuring that there is sufficient high-molecular-weight material to form the strong network and sufficient medium-molecular-weight material to stabilize the structure. The desirability of very low-molecular-weight portions is questionable, as they will serve only to increase the viscosity of the truly fluid elements of the structure, which must flow around the network on deformation of the specimen. The proper balance will be found only by experiment, but it appears that, when nonsolvent-type plasticizers are used, uniform and polymolecular materials will not have the same properties.

2. Strength and Flexibility

As soon as it became evident that cellulose derivatives could be fractionated into portions differing greatly in viscosity and other physical properties, interest was naturally aroused in the question of whether a mixture of high- and low-molecular-weight material had better or worse technical properties than a more uniform product. Cellulose derivatives were accordingly fractionated, and the strength and elongation of films or filaments made from the fractions or mixtures of them were used to characterize the products. The results of much of this early work[4, 5, 6] seemed to indicate a definite advantage of blends of high- and low-molecular-weight material over uniform fractions having the same viscosity in solution as the blends. This conclusion is diametrically opposed to that indicated by more recent work. The earlier workers seem to have been influenced by preconceived concepts based on the micellar theory. For example, Herzog and Deripasko[5] speak of the analogy with systems composed of packed spheres, where it is possible to secure a much more dense packing if a graded mixture of small and large spheres is employed than if all the spheres possess the same size. The idea that the low-molecular-

[4] For a review of this work, see H. Mark, *Paper Trade J.*, **113**, 28 (July 17, 1941). Note especially, H. J. Rocha, *Kolloidchem. Beihefte*, **30**, 230 (1930)

[5] R. O. Herzog and A. Deripasko, *Cellulosechem.*, **13**, 25 (1932).

[6] F. Ohl, *Kunstseide*, **12**, 468 (1930).

weight portions of a product act as a cementing material is found repeatedly in cellulose chemistry, but finds no support in present-day viewpoints of polymer structure, which ascribe the chief role in supporting a load to an interlocking network composed of the longer molecules. It is probable that the earlier workers made too few experiments on too poorly fractionated products actually to decide the point, especially in view of the difficulty in checking stress-strain curves for a given material within 20% in duplicate experiments. The possibility remains that, by some methods

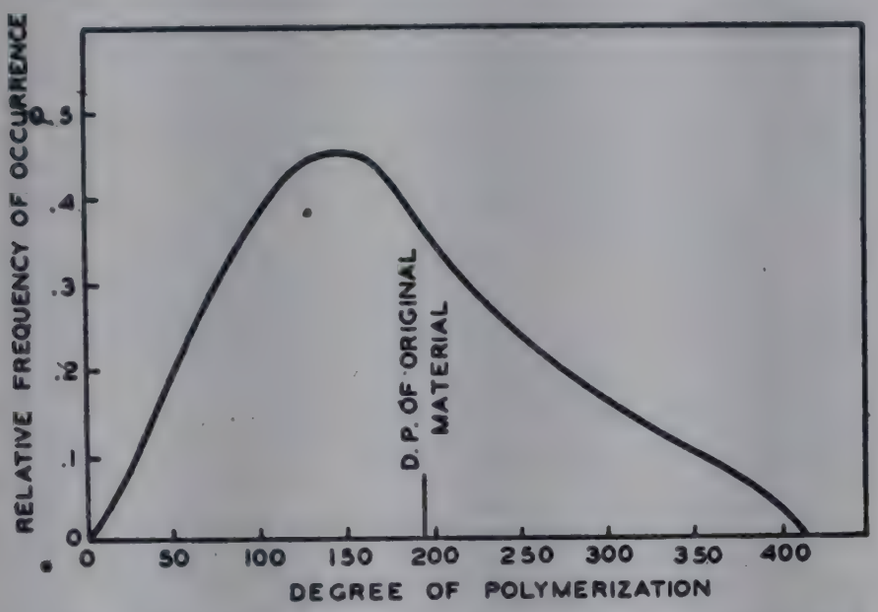

FIG. 32.—DIFFERENTIAL DISTRIBUTION CURVE FOR CELLULOSE ACETATE (WEIGHT BASIS) (SOOKNE, RUTHERFORD, MARK, AND HARRIS[9]).

of preparing films or fibers, blends may have an advantage because of the fact that the high-molecular-weight portion of the blend, which is necessarily higher in molecular weight than a uniform product of the same viscosity in solution and therefore higher in strength, may be precipitated out first, either on the surface or as a continuous network throughout the material, in such a manner that this portion occurs at the points of maximum stress, and therefore leads to better physical properties.

More recent work on this problem, using nitrocellulose[7, 8] and cellulose acetate,[9, 10] has led to the conclusion that the more uniform the product

[7] H. M. Spurlin, *Ind. Eng. Chem.*, **30**, 538 (1938).

[8] M. Wadano, *Kolloid-Z.*, **92**, 362 (1940).

[9] A. M. Sookne, H. A. Rutherford, H. Mark, and M. Harris, *J. Research Natl. Bur. Standards*, **29**, 123 (1942).

[10] A. M. Sookne and M. Harris, *J. Research Natl. Bur. Standards*, **30**, 1 (1943). The writer wishes to express his appreciation for the opportunity to examine these results before publication.

is, the better its physical properties are. As the work on cellulose acetate is the most complete and conclusive, it will be examined in detail. An acetone-soluble-type cellulose acetate of substitution 2.3 was subjected to a series of three successive fractionations. The initial precipitate, high in ash content, was discarded, and the remaining fractions were combined to give fourteen fractions. The distribution curve calculated from the molecular weights of these fractions is shown in Figure 32. Fractions and blends of fractions were cast into films, and the tensile strength,

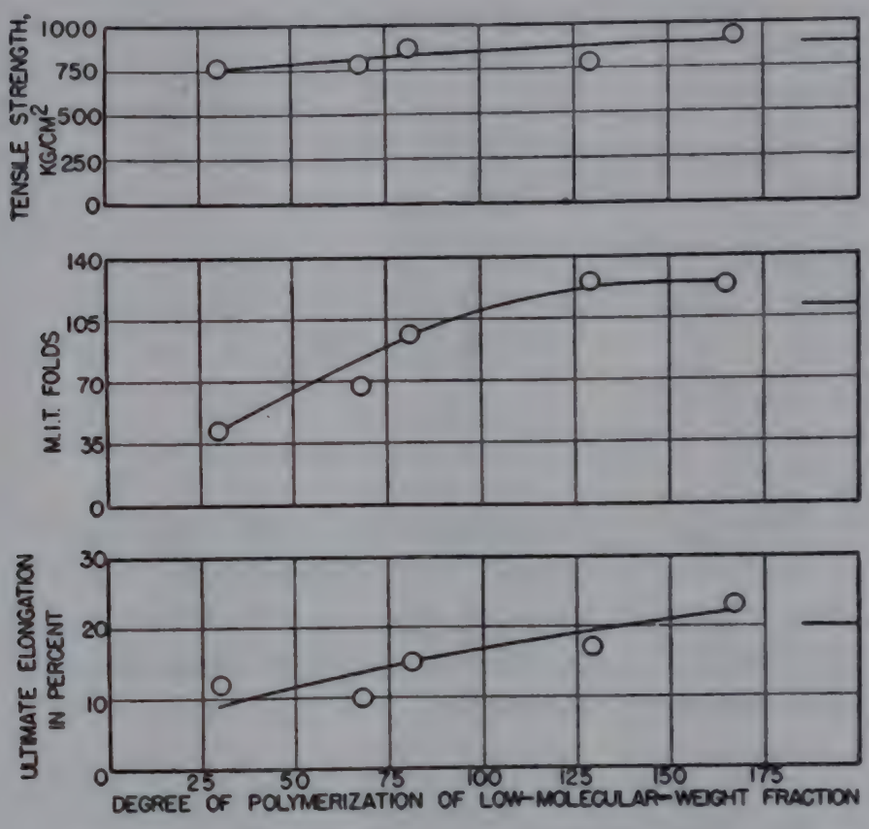

FIG. 33.—DEPENDENCE OF PHYSICAL PROPERTIES OF CELLULOSE ACETATE OF WEIGHT-AVERAGE D.P. 200 ON DEGREE OF POLYMOLECULARITY (SOOKNE AND HARRIS[10]).

The mechanical properties of a fraction of D.P. 194 are represented by the bars at the right side of the graphs.

elongation, and fold resistance were determined. On plotting the results against the viscometrically determined (weight-average) molecular weight, it was noted that for a given molecular weight the relatively uniform fractions gave the best films, and the films became progressively poorer with greater differences of molecular weights of the fractions used in preparing the blends. This behavior is illustrated in Figure 33 for blends having a weight-average D.P. of 200. In agreement with Spurlin,[7] it was found that fold resistance gave more widely varying results than

tensile strength or elongation. The further observation was then made that, if the results were plotted against number-average molecular weight (Fig. 34), there was little difference between blends and fractions.

This last fact lends support for an assumption frequently made about the nature of mechanical failure of films. According to this, films fail

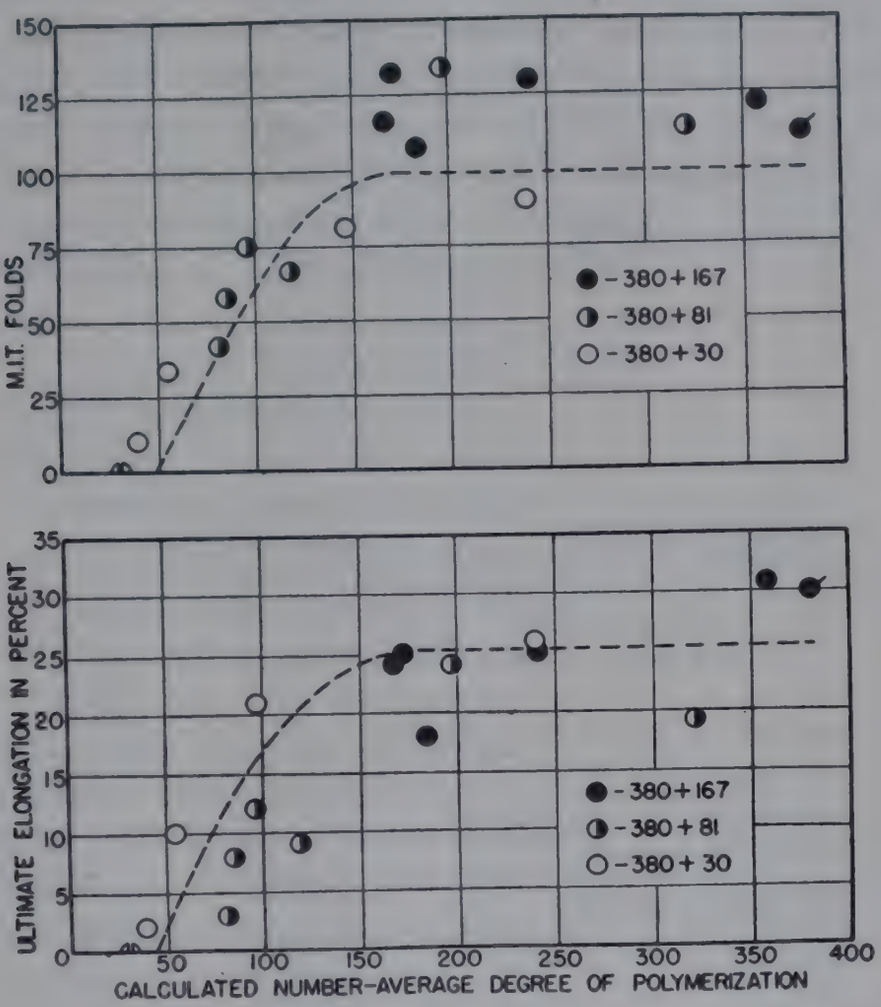

FIG. 34.—DEPENDENCE OF PHYSICAL PROPERTIES OF BLENDS OF CELLULOSE ACETATE FRACTIONS ON THE NUMBER-AVERAGE D.P. (SOOKNE AND HARRIS[10]).

The broken line is for pure fractions. The tagged circle is common to all three series of blends.

at points where chain ends are relatively concentrated, since separation of the long molecules from one another is easiest there.[11] These weak spots in the structure contain both the chain ends which occurred there by chance when the film was formed and those which move there as a result of molecules slipping along one another when an external stress

[11] K. H. Meyer, *Congr. intern. quím. pura aplicada, 9th Congr., Madrid, 1934*, **4**, 123 (1935).

is applied. For equal number-average molecular weights there will be the same number of molecule ends per unit volume, regardless of the uniformity of the polymer. Thus, it would be expected that mechanical properties which depend upon the number of chain ends close to each other would not be different for blends and fractions as long as the number-average molecular weight remained unchanged.

The lack of variation of physical properties of materials of the same number-average degree of polymerization (D.P.) with degree of polymolecularity found by Sookne and Harris[10] must be only a first approximation. For example, a blend of 75% by weight of ethylcellulose of D.P. 1000 with 25% by weight of partially ethylated glucose would have a number-average D.P. of about 4. In spite of the fact that the data in Figure 34 would indicate that a product of this D.P. would not be able to form a film, experience has shown that such compositions have quite good mechanical properties,[12] the monomer acting as a plasticizer. It may be expected that the controlling factor in determining mechanical properties will prove to be the summation over the whole volume of the substance of some function of the length of contact between neighboring chains. For example, in the model illustrated in Figure 35, perfectly uniform chains are distributed in such a manner that the maximum degree of interlocking is obtained. In Figure 36, an arrangement of the molecules in a mixture containing 25% monomer by weight, and therefore having a number-average D.P. of about 4, is depicted which allows a very considerable length of contact between the long molecules. In such an arrangement, a stress could be transmitted from one end of the system to the other without calling into play any contribution by the monomer. Of course, these structures are highly idealized, but it can be seen that the ease of slippage at any individual point in a chain is determined both by the chance that that point is far removed from a chain end on at least two of the chains surrounding that point, and by the chance that the neighboring chains in turn are in contact with still further removed ones along a considerable

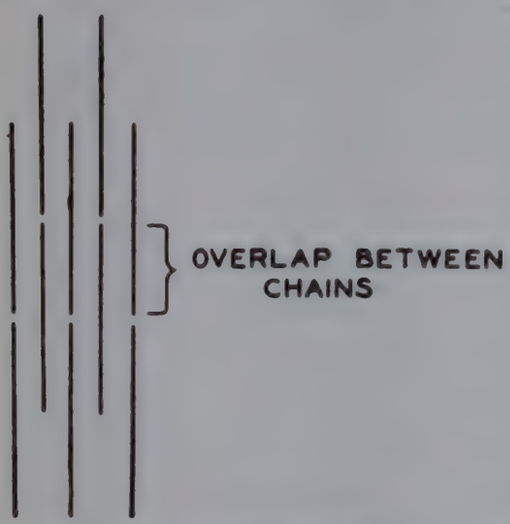

FIG. 35.—ARRANGEMENT OF UNIFORM CELLULOSE MOLECULES WHICH GIVES MAXIMUM INTERLOCKING OF CHAINS.

[12] E. V. White (to The Dow Chemical Co.), U. S. Patent 2,235,783 (Mar. 18, 1941).

portion of their length. A complication in applying statistical considerations to actual structures arises from the fact that the arrangement of the chains should be determined largely by the high-molecular-weight portions. These, because of their relatively slight mobility, will have little chance to move with respect to one another during drying of a film or molding of a plastic. The low-molecular-weight portions, on the contrary, will have a greater tendency to diffuse and fill up voids left by the immobilization of the longer chains with respect to one another. The net result will be a tendency toward segregation on a micro scale, relatively large regions being composed of the low-molecular-weight portions in localized pockets, while a continuous structure of the remaining portion exists which can support a load. Qualitative considerations favor the viewpoint

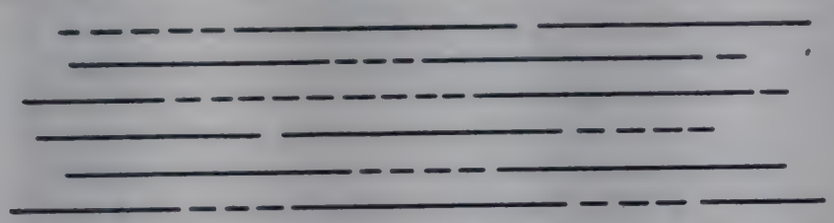

FIG. 36.—ARRANGEMENT OF A MIXTURE OF CELLULOSE MOLECULES CONTAINING 25% MONOMER BY WEIGHT IN WHICH THE LONG MOLECULES ARE INTERLOCKED TO GIVE STRENGTH TO THE STRUCTURE.

that, while the number-average D.P. will determine the mechanical properties in cases of not too great disparity in length between the large and small molecules, the weight-average D.P. will be of more importance in cases of a greater degree of polymolecularity.

From the practical standpoint, the important problem is often to secure the greatest possible strength, elongation, fold-resistance, or impact resistance for a given viscosity. The results cited lend strong support to the view that this goal is approached more nearly as the degree of uniformity is increased. However, if the viscosity is not the controlling factor, present information indicates that the optimum physical properties may be obtained by increasing the molecular weight regardless of the degree of polymolecularity; the degree of polymolecularity is then not an important consideration.

3. Technical Use of Fractionation Curves

In view of the preceding discussion, it is evident that the degree of polymolecularity of a cellulose product will be technically important because it will determine: (1) the percentage of the material lost on treatment with reagents having some solvent action, such as mercerizing baths or nitrating

mixtures; (2) the flow and knitting characteristics of the material in solution or during a molding operation; (3) the type of interaction with other ingredients of a useful composition; (4) the nature of a film-casting or filament-spinning process, especially if partial coagulation is involved during the initial steps; and (5) the physical properties of the product.

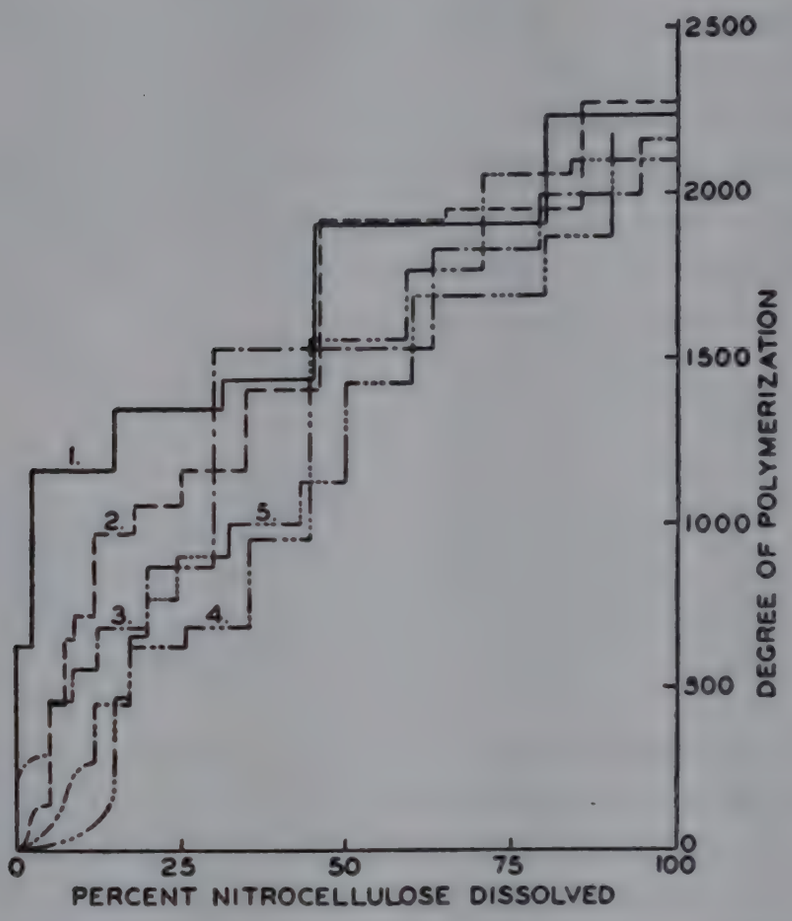

FIG. 37.—INTEGRAL FRACTIONATION CURVES FOR NITROCELLULOSES FROM VARIOUS PULPS (SCHIEBER[13]).

Curves:

1. Cotton linters (alkali-treated and bleached).
2. Sulfate pulp from pinewood (purified).
3. Sulfite pulp from pinewood (high-viscosity, purified).
4. Sulfite pulp from beechwood (high-viscosity).
5. Sulfite pulp from beechwood (normal).

Another factor which is becoming recognized is the influence on the chemical stability of the product exerted by foreign groups, such as combined sulfuric acid, which are found in largest amount in the low-molecular-weight portions.

The German staple-fiber industry is the only group which has indicated

[13] W. Schieber, *Papier-Fabr.*, **37**, Tech.-wiss. Tl., 245 (1939).

by publishing its results that it considers a determination of degree of polymolecularity of primary technical importance. These workers,[13, 14] who were confronted with the problem of evaluating pulps for the viscose process, found that nitration for one hour at 18°C. in a bath composed of 100 parts 83% H_3PO_4, 114 parts P_2O_5, and 140 parts HNO_3 (sp. gr. more than 1.52), led to no appreciable degradation. One group preferred to fractionate the nitrate by fractional extraction with alcohol-ethyl acetate

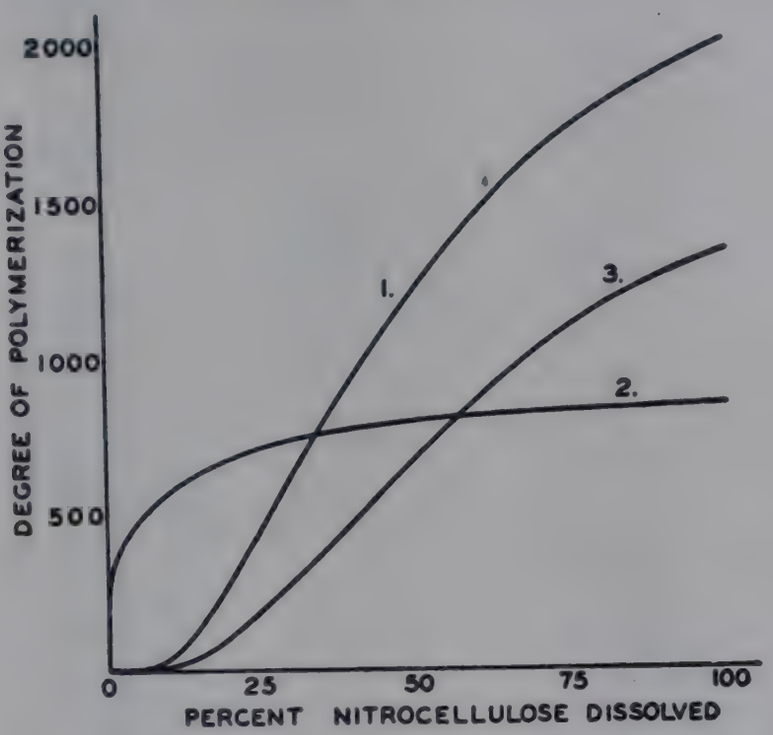

FIG. 38.—INTEGRAL FRACTIONATION CURVES FOR NITROCELLULOSES FROM VARIOUS PULPS (SCHIEBER[13]).

Curves:

1. Normal sulfite pulp.
2. Ideal viscose pulp with the same viscosity.
3. Sulfite pulp with lower viscosity.

mixtures of gradually increasing solvent power; another group dissolved the nitrate and then fractionally precipitated it. The molecular weights of individual fractions were determined by the viscosity method. Typical integral fractionation curves are illustrated in Figure 37. The small content of the low-molecular-weight material in cotton linters is quite striking when compared with that in wood pulp. After a comparison of the properties of staple fibers made from many pulps, it was concluded that the ideal

[14] H. Staudinger and J. Jurisch, *Melliand Textilber.*, **20**, 693 (1939); H. Dolmetsch and F. Reinecke, *Zellwolle u. Deut. Kunstseiden-Ztg.*, **5**, 219, 299 (1939); R. E. Dörr, *Angew. Chem.*, **53**, 292 (1940); J. Jurisch, *Chem.-Ztg.*, **64**, 269 (1940).

raw material should contain very little low-molecular-weight material, as this was deleterious, especially from the standpoint of wet strength, and that none of the remainder should be much above a D.P. of 600, as higher values gave no improvement in properties but led to processing troubles due to high viscosity. The ideal curve described by these investigators is shown in Figure 38, together with smoothed curves for sulfite celluloses.

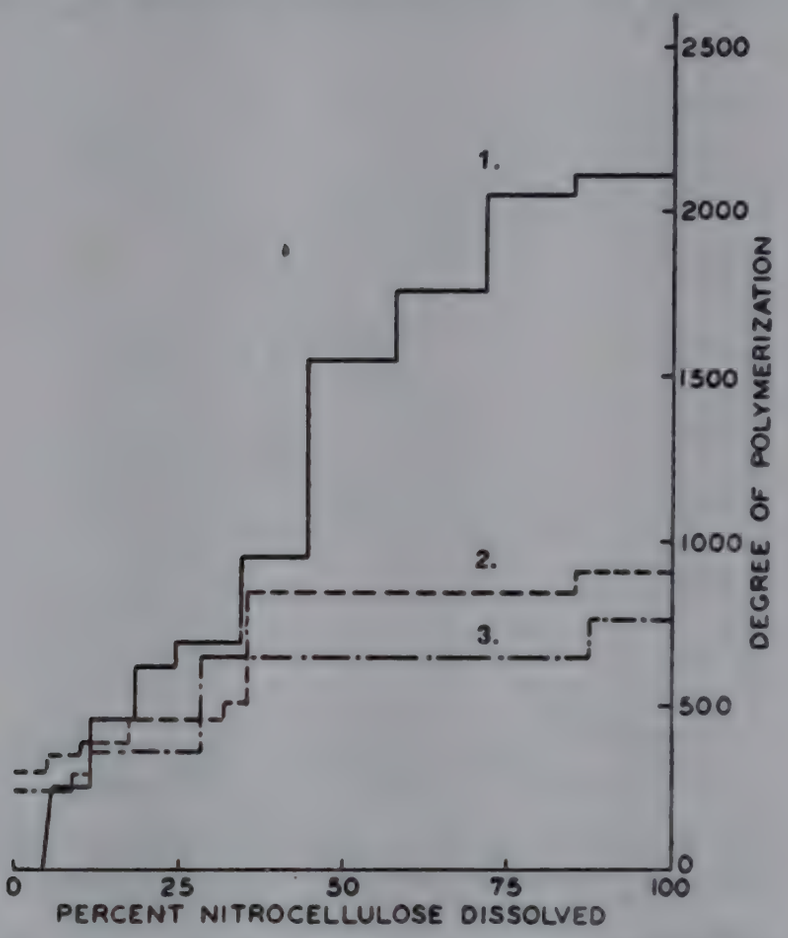

FIG. 39.—INTEGRAL FRACTIONATION CURVES FOR NITROCELLULOSES FROM VARIOUS PULPS (SCHIEBER[13]).

Curves:

1. Original beech pulp.
2. Specially treated beech pulp.
3. Staple fiber.

In Figure 39 are given actual fractionation curves of a beech sulfite pulp, a specially treated pulp, and a staple fiber, in order to demonstrate the degree to which the ideal could be approached.

In the consideration of this type of work, it must not be forgotten that commercial wood pulps are by no means pure cellulose. The hemicelluloses, especially the pentosans, have different solubility characteristics than cellulose. They will, therefore, markedly influence solubility diagrams. They are well known to have a generally undesirable influence on the

properties of cellulose products. Therefore, any evaluation of pulps should include a consideration of the effect of impurities on the method used.

A further consideration in the use of fractionation studies is the problem of evaluating the high-viscosity fraction, which contains most of the

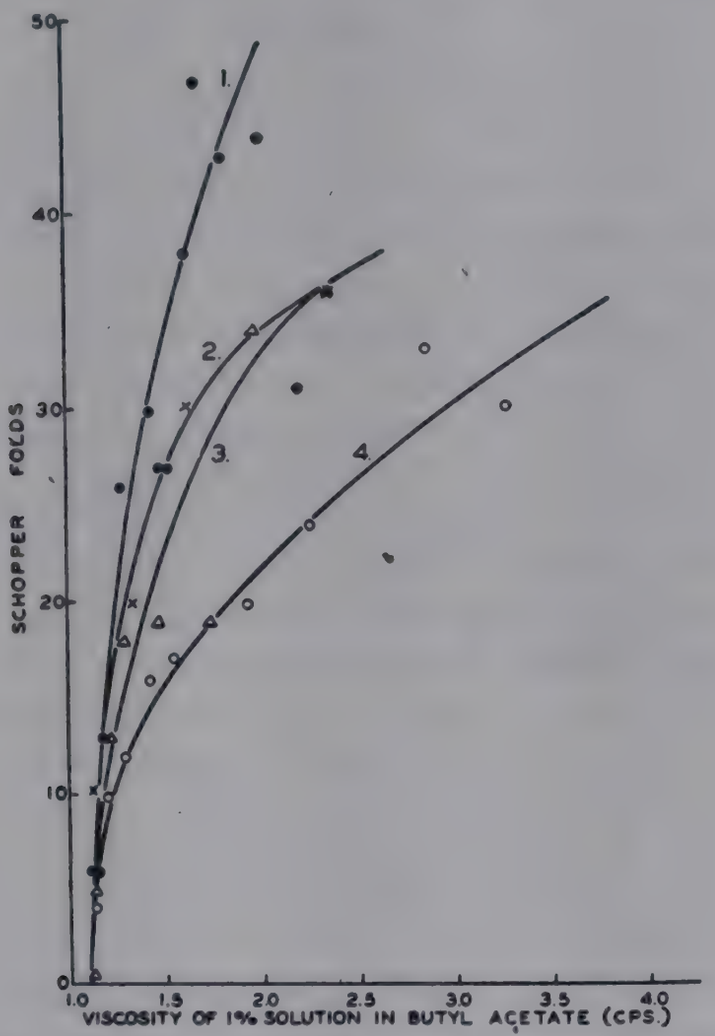

FIG. 40.—VARIATION OF FOLD RESISTANCE WITH VISCOSITY FOR NITROCELLULOSES OF DIFFERENT DEGREES OF POLYMOLECULARITY (SPURLIN[7]).

Curves:

1. ●—Fractionated nitrocelluloses.
2. ×—Commercial (unfractionated) nitrocelluloses.
3. △—Blends of 5-sec. and 15-cp. nitrocelluloses.
4. ○—Blends of 20-sec. and 15-cp. nitrocelluloses.

bound ash. This metal content leads to poor solubility and consequent difficulty in determining the molecular weight. For this reason, Harris and his coworkers,[9, 10] in the work described above, neglected the high-ash fraction. Spurlin,[7] in his work on nitrocellulose, found that the highest fraction had definitely poorer properties than would be expected from its

viscosity in butyl acetate (Fig. 40). This indicates that the poor solubility of this fraction is due to cross-linking of the type discussed in previous sections of this chapter, and that the viscosity even in as dilute a solution as 1% in the nonhydroxyl-containing solvent, butyl acetate, is not an indication of the true molecular weight.

4. Conclusion

From the foregoing discussion, it is evident that the degree of polymolecularity has to be taken into account in many technical applications. However, it may be concluded that there is little immediate possibility of sweeping improvements as a result of control of chain-length distribution in derivatives used in ordinary commercial practice. This results primarily from the expense of fractionation procedures. To the extent that fractionation is practiced at present, it involves the loss of a considerable amount of material which is discarded in purification treatments of pulps. As is clear from the discussion in Chapter II, Section I, there is no hope of degrading the originally high-molecular-weight cellulose in such a manner as to secure a uniform chain length. Also, it has not as yet been demonstrated that the undoubted improvements that can be achieved in such products as artificial silk by elimination of low-molecular-weight portions of the cellulose can not be more economically secured by modifying the fabrication process so that raw materials of higher average molecular weight, and therefore lower inherent content of small molecules, can be used. It appears probable that progress in cellulose utilization is most likely from improvement in refining operations so that the content of hemicelluloses, waxes, pectin, etc., as well as chemically bound groups such as carboxyl and carbonyl, is reduced. Fractionation, on the contrary, may be expected to be advantageous only if outlets for all of the fractions are found, and the process of fractionation is much improved.

E. THEORY OF THE VISCOSITY OF DILUTE SOLUTIONS OF LONG-CHAIN COMPOUNDS

MAURICE L. HUGGINS

The importance of the viscosity of solutions of long-chain compounds results chiefly from the fact that viscosity measurements on such solutions are commonly used for the purpose of estimating average molecular weights. The customary procedure has involved the noncritical use of an empirical relation (equation 12) which certainly is approximately correct in many instances, but which, just as certainly, is often quite inaccurate. It is the purpose of this section to examine the theoretical basis for this and related equations, in order to give some understanding of the factors involved and of the limitations of the relationships used.

The viscosity, η, of a liquid may be defined as the force per unit area required to maintain a unit velocity gradient between two parallel plates kept a constant distance apart:

$$\eta = \frac{\dfrac{\text{force}}{\text{area}}}{\dfrac{\text{difference in velocity}}{\text{distance between plates}}} \tag{1}$$

The viscosity may also be defined as the kinetic energy transformed into heat, per unit of time and per unit volume of liquid, divided by the square of the velocity gradient:

$$\eta = \frac{\dfrac{\text{energy transformed}}{\text{time} \times \text{volume}}}{\left(\dfrac{\text{difference in velocity}}{\text{distance between plates}}\right)^2} \tag{2}$$

The fluidity, ϕ, is the reciprocal of the viscosity:

$$\phi = \frac{1}{\eta} \tag{3}$$

The specific viscosity (η_{sp}) is the difference between the viscosity of the solution (η) and that of the pure liquid solvent (η_0), divided by the latter:

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{\eta}{\eta_0} - 1 \tag{4}$$

1. Effect of Shape of Solute Molecules

(a) *Spherical and Ellipsoidal Solute Molecules*

Einstein[1] has treated theoretically the case of a dilute solution (or suspension) containing spherical solute (or suspended) particles which are large relative to the size of the solvent molecules. These large spheres block the motion of some of the solvent molecules and so produce an increase in viscosity. The quantitative relation is

$$\eta_{sp} = \frac{5}{2} V_2 \tag{5}$$

where V_2 is the volume fraction of the solute (or suspended material). Guth, Simha, and Gold,[2, 3, 4] extending Einstein's hydrodynamic treatment to take account of the mutual interference of the solute particles, have obtained the relation:

$$\eta_{sp} = \frac{5}{2} V_2 + 14.1 V_2^2 \tag{6}$$

It should be emphasized that these relationships depend on the assumption of *large spherical* solute (or suspended) particles. For solute and solvent particles of the same size (and with solvent-solvent and solvent-solute attractions equal), the viscosity of the solution is obviously identical with that of the pure liquid solvent; that is,

$$\eta_{sp} = 0 \tag{7}$$

For spherical solute particles of intermediate size, the specific viscosity should be intermediate between that corresponding to equation (6) and zero, as given by equation (7).

Solutions and suspensions containing relatively large *ellipsoidal* particles have been dealt with theoretically by various authors.[5–8] The problem is a very difficult one, and a reasonably satisfactory result has been obtained only for the limiting case of such strong Brownian motion (or such small velocity gradients) that all orientations of the ellipsoids are equally

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[1] A. Einstein, *Ann. Physik*, **19**, 289 (1906); **34**, 591 (1911).
[2] E. Guth and R. Simha, *Kolloid-Z.*, **74**, 266 (1936).
[3] E. Guth and O. Gold, *Phys. Rev.*, **53**, 322 (1938).
[4] E. Guth, *Proc. 5th Intern. Congr. Applied Mechanics* (1938).
[5] G. B. Jeffery, *Proc. Roy. Soc. (London)*, **A102**, 161 (1922).
[6] R. Eisenschitz, *Z. physik. Chem.*, **A158**, 78 (1931); **A163**, 133 (1933).
[7] E. Guth, *Kolloid-Z.*, **74**, 147 (1936)
[8] R. Simha, *J. Phys. Chem.*, **44**, 25 (1940).

probable. For prolate ellipsoids, with the axial ratio f very large, the result[8] obtained is

$$\eta_{sp} = V_2\left(\frac{f^2}{15 \ln 2f - \frac{45}{2}} + \frac{f^2}{5 \ln 2f - \frac{5}{2}} + \frac{14}{15}\right) \tag{8}$$

This equation must be very inaccurate for solute molecules of about the same size as the solvent molecules—just as equations (5) and (6) are very inaccurate under such circumstances. For large solute molecules, the question as to whether the Brownian motion is more potent in determining the distribution of ellipsoid orientations than is the velocity gradient becomes very important. Only if the measured viscosity is shown to be independent of the velocity gradient is one justified in considering equation (8) a good approximation.

Equally important, as regards the possible application of this equation to solutions of macromolecules, is the question as to whether the actual shape of the solute molecules is well enough approximated by an ellipsoid. It would, perhaps, not be unreasonable to assume this, as a first approximation, for fully extended zigzag chains or for "globular" proteins, but to assume that an ellipsoid is even a fair approximation for a kinked-chain molecule seems pretty far-fetched. Since most or all of the macromolecules which are discussed in this book are known to be kinked, rather than rodlike, in solution (see below), it must be concluded that equation (8) is not very useful for our purposes.

(*b*) *Rodlike and Kinked-Chain Solute Molecules*

Kuhn[9] has made a theoretical study of hypothetical solutions in which each solute molecule is rodlike, composed of a straight chain of spheres, with the distance (l) between adjacent sphere centers equal to four times the radius (a) of each. He computed, as a function of the dimensions and orientation of such a molecule and of the velocity gradient in the solution, the difference in velocity between the center of each spherical "submolecule" and the liquid bathing it. Using Stokes' law, he then obtained the contribution of this submolecule to the viscosity of the solution. (This involved the assumption that the streaming of the liquid past one submolecule is not significantly affected by the presence of adjacent submolecules.) Summing over all the submolecules and over all orientations gave the total viscosity effect due to the solute molecules.

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[9] W. Kuhn, *Z. physik. Chem.*, **A161**, 427 (1932).

Kuhn's treatment has been corrected and generalized by Huggins,[10] who obtained the following limiting equation for very long rods, assumed to be oriented in a random way (that is, assuming the Brownian motion to be much more effective than the velocity gradient in determining the distribution of orientations):

$$\eta_{sp} = \left(\frac{\pi N}{24{,}000}\right) l^2 a n^2 c \tag{9}$$

Here, N denotes Avogadro's number, n the number of spheres of radius a ("submolecules") in each rod (molecule), l the distance between centers of adjacent submolecules, and c the concentration in "submoles" per liter. In dilute solutions c is proportional to the volume fraction, V_2.

For the other limiting case, in which the orientation distribution is determined entirely by the velocity gradient, the result obtained by Huggins was

$$\eta_{sp} = k_E V_2 \tag{10}$$

where k_E has a value (usually less than 5/2) which depends on the relative sizes and shapes of the solute and solvent molecules (cf. equations (5) and (7)). For long rodlike solute molecules, the specific viscosity according to equation (10) is negligible compared with that according to equation (9). For solutions of rodlike molecules, therefore, as also for the ellipsoidal case discussed above, there should be a very great dependence of the viscosity on the velocity gradient.

Huggins has also treated solutions of chain molecules which are kinked in a purely random way, except that the angle between the bonds joining adjacent submolecules (considered, for simplicity, as spheres) is assumed to be uniform and constant. The limiting equation obtained, for n large, is

$$\eta_{sp} = kBl^2 anc \tag{11}$$

In this equation, as before, c is the concentration in submoles per liter, n is the number of spherical "submolecules," of radius a, in each molecule, and l is the distance between the centers of adjacent submolecules. B is a quantity which depends on the constant angle between the two bonds joining each submolecule to its two neighbors; for tetrahedral angles it has the value 2. The constant k has the value 2.94×10^{20} for the extreme case of strong Brownian motion or small velocity gradient, and 2.82×10^{20} for the other extreme of weak Brownian motion or large velocity gradient. Since the difference between these two values is small, for this model (and for actual solutions approximated by it) the viscosity depends only slightly on the velocity gradient in the solution.

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[10] M. L. Huggins, *J. Phys. Chem.*, **42**, 911 (1938); **43**, 439 (1939).

From the above relationships, it may be concluded that, if the solute molecules are large relative to those of the solvent and if the Brownian motion predominates over the velocity gradient in determining the distribution of solute molecule orientations, the ratio of specific viscosity to concentration (c or V_2) for a homologous series (n variable; B, l, and a constant) is:

(1) constant for spherical solute molecules,
(2) proportional to n^2 for rodlike solute molecules, and
(3) proportional to n for randomly kinked solute molecules.

The last of these relations is that discovered empirically by Staudinger[11]; that is,

$$\frac{\eta_{sp}}{c} = k_n n \tag{12}$$

It is known to hold approximately for many types of long-chain compounds, although (as would be expected) significant deviations are observed, especially for small values of n.

Because of this correspondence, because of the general agreement between the thermodynamic properties of solutions of long-chain molecules with equations derived on the assumption that the solute molecules are very much kinked (see Section B of this chapter), and because of various theoretical arguments which need not be discussed here, it seems certain that, in solutions of most natural and synthetic polymers, the solute molecules are convoluted in a more or less random way.

2. Effect of Other Variables

(a) *Dependence of Viscosity on Solute Variables*

Comparing equation (11) with equation (12), one sees how the proportionality constant k_n in the Staudinger relationship should vary with certain characteristics of the *solute* molecule. If the chain is one with really free rotation at equally spaced joints, the segments (submolecules) between joints being rigid, l may be taken as the distance between joints, a as the radius of a hypothetical sphere which would produce the same viscosity increase (when in the same environment) as a single segment, and B as the constant corresponding to the angle between the straight lines connecting each joint with the two adjacent joints. Since most of the chain molecules which are of interest do not consist of rigid segments with free rotation

[11] H. Staudinger, *Die hochmolekularen organischen Verbindungen*. J. Springer, Berlin, 1932.

at the joints between them, l, a, and B must be taken as representing effective average dimensions. Comparison of empirical values of k_n for appropriate solutes should furnish useful information about the variation of these effective dimensions with the molecular formulas.

Equation (11) was derived for a model for which perfect flexibility was assumed at each joint in the chain. It is pertinent to inquire whether or not it is valid for solutions of actual chain molecules in which the flexibility is far from perfect. There is neither *free* rotation about the single bonds in the chain nor are the chains entirely rigid. Careful consideration of this problem has led the writer to conclude that the proportionality between η_{sp} and nc should still hold, but with a different value for the proportionality constant, that is, the effective kBl^2a product.

(*b*) *Dependence of Viscosity on Solvent Variables*

The effect of the properties of the *solvent* molecules will now be considered. Qualitatively,[12–14] it is obvious that the solute chains will, on the average, be more tightly coiled than in purely random kinking if the average cohesion energy (or, better, energy *density*) between *like* units, that is, between two solute submolecules (not directly bonded together) and between two solvent molecules, is greater than that between *unlike* units: one solute submolecule and one solvent molecule. This will result in a lower viscosity for a given value of n than that which is in accord with equation (11); also, the ratio η_{sp}/cn will decrease, rather than stay constant, as n increases. On the other hand, if (describing the situation crudely) unlike units, rather than like units, prefer to be adjacent to each other, the solute chain molecules will, on the whole, be extended more than in the perfectly random case; the viscosity at a given n value will be greater than that given by equation (11); and the ratio η_{sp}/cn will increase as n increases.

A measure of the difference between the average cohesive energy density between like molecules and that between unlike molecules is the constant α_1 in the approximate expression

$$\bar{L}_1 = \alpha_1 V_2^2 \tag{13}$$

for the heat of solution of the solvent molecules. In general, α_1 is symbatic with μ_1. [If α_1 increases (or decreases), μ_1 also increases (or decreases).] This (μ_1) is the important constant, characteristic of the components of

[12] M. L. Huggins, *J. Applied Phys.*, **10**, 700 (1939).
[13] P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).
[14] T. Alfrey, A. Bartovics, and H. Mark, *J. Am. Chem. Soc.*, **64**, 1557 (1942).

the solution, which enters into the equations discussed above (Section B of this chapter) for the activities, osmotic pressures, solubilities, etc., of solutions of chain molecules. The larger μ_1 is, the smaller is the proportion of nonsolvent needed to cause the separation of a second phase. [In the terminology of equations (23) to (25), in Section B, the larger μ_b is, the smaller is V_a' in the saturated solution.]

TABLE 1

COMPARISON OF VISCOSITY CONSTANTS OF POLYBUTENE SOLUTIONS WITH THEIR "ALCOHOL NUMBERS" (EVANS AND YOUNG[16])

Solvent	$\frac{\eta_{sp}}{c}$	Alcohol number
Isoamyl butyrate	0.057	0.0
Isoamyl caproate	0.150	1.8
Benzene	0.221	14.6
Toluene	0.429	20.3
Xylene	0.678	21.7
n-Propylbenzene	0.690	21.7
Mesitylene	0.690	21.8
Cymene	0.714	21.9
Amylbenzene	0.784	22.0
n-Hexane	0.530	22.9
n-Heptane	0.855	26.4
n-Octane	0.923	26.5
Varsol No. 2	1.018	31.8

From this line of argument, it may be concluded that, except for minor complications, the magnitude of the ratio η_{sp}/c for a given long-chain solute (n constant) in different solvents should be symbatic with the amount of nonsolvent which must be added to cause the formation of a new phase. This relationship has been observed, for example, by Staudinger and Heuer[15] for polystyrene solutions and by Evans and Young[16] for polybutene solutions.

Table 1 shows some results obtained by the latter pair of authors. The measurements were made on solutions of polybutene of estimated average molecular weight 104,000. The concentration, c, was 10 g./l. in each case. The viscosity measurements were at 25°C., the alcohol number determinations at "room temperature." The alcohol number is here defined as the number of cc. of 2-ethylbutyl alcohol required to produce 400% relative

[15] H. Staudinger and W. Heuer, *Z. physik. Chem.*, **A171**, 129 (1934).

[16] H. C. Evans and D. W. Young, *Ind. Eng. Chem.*, **34**, 461 (1942).

turbidity in 25 cc. of polymer solution. The isoamyl butyrate solution was turbid without the addition of any alcohol; it was agitated before the viscosity was measured.

(c) *Dependence of Viscosity on Concentration*

In both Kuhn's and Huggins' derivations of viscosity equations, Stokes' law,

$$\text{Force} = 6\pi\eta a u \tag{14}$$

was assumed in computing the frictional force acting on each submolecule as a result of its velocity (u) relative to the immediately surrounding liquid. The insertion of η_0, the viscosity of the pure solvent, for η in this equation leads to the limiting equations (9) to (12) given above. These must therefore be considered to be strictly applicable only to infinitely dilute solutions; that is,

$$\left(\frac{\eta_{sp}}{c}\right)_{c=0} = k_n n, \text{ etc.} \tag{15}^{16a}$$

If one inserts into equation (14) the value of the viscosity of the *solution*

$$\eta = \eta_0(1 + \eta_{sp}) \tag{16}$$

the equation

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0}(1 + \eta_{sp}) \tag{17}$$

is obtained. For small concentrations this is equivalent to

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0} + \left(\frac{\eta_{sp}}{c}\right)^2_{c=0} c \tag{18}$$

At first sight, it might seem that this should give the initial variation of η_{sp}/c with concentration. The application of equation (14) to the solutions under discussion is, however, very questionable. This equation would be applicable, strictly speaking, only if each submolecule were isolated from all others, so that the liquid streaming past one would not be affected by the disturbances of the streaming around other submolecules. Moreover, the use of this equation involves the assumptions that the submolecules are spherical and are large relative to the solvent molecules, also that there is no sliding friction, as the solvent molecules move around the submolecules. It certainly does not seem proper, in calculating the dissipation of energy when a *solute* submolecule interacts with the surrounding (chiefly *solvent*) molecules, to use a value of η which is related primarily to the mutual interaction between *solvent* molecules.

[16a] $\left(\frac{\eta_{sp}}{c}\right)_{c=0} = \left(\frac{ln(\eta/\eta_0)}{c}\right)_{c=0}$. This ratio, with the concentration in grams per 100 ml., is frequently called the intrinsic viscosity and designated by $[\eta]$. See Ref. 25.

It seems reasonable to assume that these objections to the use of equation (14) can all be met, approximately, by the introduction in it of another factor (k', usually a fraction) having a magnitude characteristic of the system being considered, depending on the sizes, shapes, and cohesional properties of both solvent molecules and solute submolecules, but not on the number of submolecules (that is, the length) of the solute molecule chain. Thus, equation (14) is replaced by

$$\text{Force} = 6\pi k'\eta a u \tag{19}$$

This leads to

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0}(1 + k'\eta_{sp}) \tag{20}$$

which is identical with an empirical equation recently published by Schulz and Blaschke[17] and tested by them on polymethyl methacrylate solutions in chloroform. The same value of k' (0.30) was found satisfactory for the unfractionated polymer and for each fraction studied.

Equation (20) can readily be put into the form

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0} + k'\left(\frac{\eta_{sp}}{c}\right)_{c=0}^{2} c + \text{terms in higher powers of } c \tag{21}$$

the higher terms being negligible for dilute solutions. This form is especially well suited for comparison with the many other equations which have been proposed to represent the variation with concentration of the viscosity of solutions. Nearly all of them can be expanded into an expression of this sort; they differ only with respect to the value and interpretation of k' and with respect to the higher terms. Although there is not space for an exhaustive comparison of these various equations, a few will be mentioned. (See also Section F of this chapter, especially Table 2.)

Martin,[18] considering data for solutions of a wide variety of high-molecular-weight solutes in various solvents, has concluded that the relation

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0} \exp\left[k_M\left(\frac{\eta_{sp}}{c}\right)_{c=0} c\right] \tag{22}$$

represents accurately viscosity-concentration relationships up to concentrations of 5%, the constant k_M varying with solvent and with solute, but being constant for members of a given polyhomologous series dissolved in a given solvent. This equation reduces to equation (21), when the higher terms in the expansion of the exponential are neglected, thus confirming the theoretical argument outlined above.

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[17] G. V. Schulz and F. Blaschke, *J. prakt. Chem.*, **158**, 130 (1941).

[18] A. F. Martin, Am. Chem. Soc. meeting, Memphis, April 23, 1942.

The equations

$$\frac{\eta}{\eta_0} = (1 + k_B c)^{k_B'} \tag{23}$$

$$\eta_{sp} = \frac{k_F k_F' c}{1 - k_F' c} \tag{24}$$

$$\eta_{sp} = k_J c e^{k_J' c} \tag{25}$$

have been proposed by Baker,[19] by Fikentscher and Mark,[20] and by de Jong, Kruyt, and Lens,[21] respectively. Here k_B, k_B', k_F, etc., are empirically determined constants. These equations all reduce to equation (21), with k' equal to $\frac{1}{2} - \frac{1}{2k_B'}$, $\frac{1}{k_F'}$, and $\frac{k_J'}{k_J}$, respectively.

Arrhenius,[22] Hess and Philippoff,[23] and Bredée and de Booys[24] have proposed the following equations, respectively:

$$\ln\left(\frac{\eta}{\eta_0}\right) = k_A c \tag{26}$$

$$\frac{\eta}{\eta_0} = \left(1 + \frac{k_H c}{8}\right)^8 \tag{27}$$

$$\frac{\eta}{\eta_0} = \left(1 + \frac{5 k_B c}{12}\right)^6 \tag{28}$$

The last two are special cases of Baker's equation (equation (23)). All three reduce to equation (21), with k' equal to $^1/_2$, $^7/_{16}$, and $^5/_{12}$, respectively, constants independent of the solvent-solute system. As would be expected, these inflexible equations do not give as good general agreement as do equation (20) and equations (22) to (25), which contain an additional adjustable constant.

It should be noted that the comparison of these various equations for the concentration dependence of viscosity has concerned only the initial slope of the $\frac{\eta_{sp}}{c}$ versus c curve and so applies only to quite dilute solutions. There will be no discussion here of the theoretical or empirical treatment of this dependence at higher concentrations, except one remark:

If the attractions between *like* molecules in the solution are considerably

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[19] F. Baker, *J. Chem. Soc.*, **103**, 1653 (1913).

[20] H. Fikentscher and H. Mark, *Kolloid-Z.*, **49**, 135 (1930).

[21] H. G. de Jong, H. R. Kruyt, and W. Lens, *Kolloid-Beihefte*, **36**, 429 (1932).

[22] S. Arrhenius, *Medd. Vetenskapakad., Nobelinst.*, **4**, 13 (1916).

[23] K. Hess and W. Philippoff, *Ber.*, **70B**, 639 (1937).

[24] H. L. Bredée and J. de Booys, *Kolloid-Z.*, **79**, 31 (1937).

more potent than those between *unlike* molecules, as indicated by a large value of μ_1 (see Section B of this chapter) and by a separation into two phases at sufficiently high concentrations, the solute molecules tend to form aggregates at concentrations somewhat below that at which the second phase begins to appear. This results in a viscosity-concentration curve with a slope which decreases (or even becomes negative) at the higher concentrations. Solutions of polybutene in *n*-butyl ether at 20°C., for example, show this effect.[16] As would be expected, the anomalous behavior disappears as the temperature is raised; μ_1 is decreased and the aggregates are dissociated.

3. Relationship of Molecular Weight to Viscosity

Since the molecular weight M of a long-chain molecule is proportional to the number n of submolecules of which it is composed, equation (12) is equivalent to

$$\frac{\eta_{sp}}{c} = K_M M \tag{29}$$

A great many "molecular-weight determinations" have been made by assuming this relationship, using a K_M value (for a given homologous series of compounds dissolved in a given solvent), computed from viscosity measurements on a sample whose molecular weight had been determined in some other way; for example, from osmotic-pressure measurements.

This procedure obviously gives incorrect results if Staudinger's rule does not hold. It has been shown above that it would not be expected to hold accurately except when the kinking of the solute molecules is perfectly random, which is not usually the case. Ample experimental evidence supports this conclusion. Further studies of the relationships between the deviations from Staudinger's rule and the magnitudes of the heat of mixing constant (α_1) and of μ_1 may make it possible to determine the course of the η_{sp}/c versus M curve for a given type of system indirectly. For the present, however, the only sure way is to obtain several well-spaced points on the curve by measuring viscosities of solutions of suitable samples whose molecular weights have been accurately determined, by osmotic measurements or otherwise. From the theoretical treatment outlined above, one may guess that these curves, if properly determined, will conform well to the relation

$$\left(\frac{\eta_{sp}}{c}\right)_{c=0} = K_0 + K_1 M^p \tag{30}$$

with K_0 a small constant, negligible except for small values of M, and ν a constant which for most types of high-polymer solutions is not very different from one.

As indicated in this equation, the limiting value, for $c = 0$, of the ratio η_{sp}/c should be used, if accurate results are desired. If equation (29) is accurate for infinitely dilute solutions of a given class, the more complicated relation,

$$\frac{\eta_{sp}}{c} = K_M M + k' K_M M^2 c + \text{further terms} \qquad (31)$$

(derived by combining equation (29) with (18)) should hold for (not too large) finite values of c. Staudinger's rule cannot be accurate both at infinite dilution and at finite (not negligibly small) concentrations. The equation for η_{sp}/c deduced by combining equation (30) with (18) likewise contains a term in $M^{2\nu}c$.

Ideally, in deducing a curve showing the dependence of η_{sp}/c on M, the samples used for the purpose should be perfectly homogeneous as regards molecular sizes (chain lengths). This is because, as Kraemer and Lansing[25] have pointed out, osmotic pressure and related methods of molecular-weight determinations give, for a mixture of molecules of different sizes, a result which is a "number-average" of the individual weights, whereas the viscosity method (assuming equation (29) to hold) gives a "weight-average."

The number-average is the ordinary type of average; to obtain a weight-average, the contribution of each molecule is "weighted" in proportion to its weight. For example, a mixture of two molecules of weight 100 units and one of weight 400 units has a number-average molecular weight of $\frac{2 \cdot 100 + 1 \cdot 400}{2 + 1} = 200$, while the weight-average molecular weight is $\frac{2(100)^2 + 1(400)^2}{2 \cdot 100 + 1 \cdot 400} = 300$. It is seen that the number-average gives relatively more importance to the smaller molecules, the weight-average to the larger molecules.

If heterogeneous samples are used to determine the η_{sp}/c versus M curve (or the constants for it) for a given system, the curve obtained is higher (K_M of equation (29) or K_1 of equation (30) will be larger) than it really should be and the (average) molecular weights computed for other samples from this curve are lower than the true weight averages.

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[25] E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 153 (1935).

Flory[26] has shown that for a "normal" distribution of molecular weights, such as exists in a synthetic polymer sample obtained by one of the usual polymerization or condensation methods, the ratio of the weight-average to the number-average is practically constant (= 2) except for very short chains. This means that the η_{sp}/c versus M curve might be calibrated with osmotic or similar data on samples having a normal distribution and used to obtain (average) molecular weights of other samples also having the normal distribution; the averages so determined would be *number* averages. A similar procedure could probably be followed with solutions of cellulose derivatives, if one could show that the distribution of chain lengths is substantially the same in the samples used for calibration and in all the "unknown" samples whose average molecular weight is desired, but this would have to be justified, before one could be sure that the results represented true number-average molecular weights.

One further point should be mentioned in connection with this molecular-weight problem: In using osmotic or cryoscopic measurements to calibrate the viscosity-molecular weight curve, the simple formulas used for small molecular solutions are not directly applicable, except at infinite dilution. As shown in Section B of this chapter, solutions of long-chain compounds usually show large deviations from Raoult's law and from relationships based on it, even when very dilute. The only legitimate procedure is to extrapolate the results to infinite dilution, for example, by plotting Π/c against c.

Of the theoretical equations which have been derived for solutions of particles of various assumed shapes, the only one which appears to be at all applicable to solutions of ordinary natural or synthetic polymers is that derived on the assumption that the solute molecules are chainlike and kinked in a random manner. The equation so deduced, like Staudinger's empirical relation, shows a proportionality (at infinite dilution) between η_{sp}/c and the chain length (or the molecular weight).

With the theoretical treatment as a basis, the dependence of η_{sp}/c on the structural characteristics of the solute molecules, on the nature of the solvent, and on the concentration of the solution has been discussed in some detail.

Finally the use of solution viscosity measurements to determine the average molecular weights of the solute molecules has been critically discussed.

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[26] P. J. Flory, *J. Am. Chem. Soc.*, **62**, 1057 (1940).

F. PRACTICAL APPLICATIONS OF VISCOSITY

G. H. Pfeiffer and R. H. Osborn

The viscosity of an ordinary liquid is associated with interactions of the nature of van der Waals' forces between its molecules, and is, therefore, a measure of internal friction. Outward manifestations of this physical property are the flow characteristics of the liquid, which are the means by which viscosity is measured.

Sir Isaac Newton was the first to express a mathematical relationship between the observable properties describing the flow of ordinary solutions. His fundamental postulate stated that the shearing stress between two adjacent liquid planes is proportional to the relative velocities of the two planes. In the case of steady flow between parallel planes,

$$S = \eta \frac{dv}{dx} \tag{1}$$

where S is the shearing stress, η is the coefficient of viscous flow (commonly known as "viscosity"), v is the velocity, and x is the perpendicular distance measured from one of the planes. The application of this relationship to actual measurements is discussed later (p. 975 *et. seq.*).

1. Viscosity of Solutions Exhibiting Anomalous Flow

(*a*) *Effect of Rate of Shear*

Certain classes of materials, which include cellulose and its derivatives, together with other highly polymerized substances such as polystyrene, rubber, starch, and proteins, form solutions which have abnormally high viscosities even in very low concentrations. These materials in 1% solution may have viscosities of the order of magnitude of thousands of times those of their solvents, while similar solutions of the so-called Newtonian liquids have viscosities only a few per cent above those of the solvents. Not only is the viscosity in these cases high, but very often it is anomalous in that the apparent viscosity is not a constant, but is a function of the rate of flow. Such anomalous behavior may be illustrated by means of a flow curve, that is, a curve which relates velocity of flow of the solution through a capillary

tube to the shearing stress (or pressure) required to produce the flow. In Figure 41 are shown typical flow curves for a true solution and for an anomalous solution, as determined by Philippoff and Hess.[1] A log-log scale is used so that detail will not be obscured at the foot of the curve. The true solution exhibits a straight-line relationship between velocity of flow and pressure, that is, constant viscosity at all pressures (up to those at which

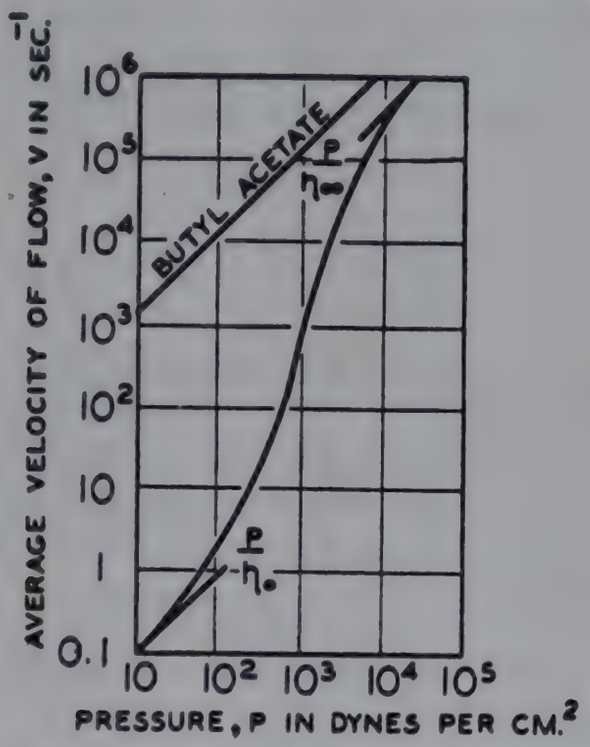

FIG. 41.—FLOW CURVE OF A 1% SOLUTION OF CELLULOSE TRINITRATE (FROM UNBLEACHED RAMIE) IN BUTYL ACETATE (PHILIPPOFF[2]).

η_0, η_∞ = Apparent viscosity at low and high shearing stresses, respectively.

turbulent flow takes place), while the curve for the anomalous solution has a typical S shape with a consequent variation of viscosity with pressure. In the latter case, it is hardly proper for us to speak of viscosity at all, because our fundamental postulates involve the idea of its constancy. Hence, in the case of substances exhibiting anomalous flow, the quantity measured in a viscometer is often designated "apparent viscosity." Ostwald[3] has used the term "structure viscosity" to describe the anomalous flow characteristics of such materials.

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[1] W. Philippoff and K. Hess, *Z. physik. Chem.*, **B31**, 237 (1936).
[2] W. Philippoff, *Cellulosechem.*, **17**, 57 (1936).
[3] Wo. Ostwald, *Kolloid-Z.*, **36**, 99 (1925); **47**, 176 (1929).

Eyring and his coworkers,[4–7] treating the problem of viscosity in liquids by the theory of reaction rates, have succeeded in explaining qualitatively the phenomenon of structural viscosity on a theoretical basis. The movement of one liquid layer past another is assumed to take place by means of individual molecules moving from one equilibrium position to another in a series of discrete jumps. In order for such jumps to occur, holes must be present in the liquid. The movement of a molecule may be considered as a transition over a potential barrier, and thus the phenomenon may be treated statistically. The following equation for viscosity was developed:

$$\eta = \frac{\frac{h}{\lambda^3}\frac{F_n}{F_a}e^{E_a/kT}}{1 + \frac{1}{6}\left(\frac{f\lambda^3}{2kT}\right)^2 + \frac{1}{120}\left(\frac{f\lambda^3}{2kT}\right)^4 + \cdots\cdots} \tag{2}$$

where f is the shearing stress between adjacent molecular layers, λ is the distance between molecules, h is Planck's constant, k is Boltzmann's constant, E_a is the energy of activation, T is the absolute temperature, F_n is the partition function associated with the normal state of the molecule, and F_a is the partition function associated with the activated state (one translational degree of freedom omitted) of the molecule.

For values of $\frac{f\lambda^3}{2} \ll kT$, the denominator of equation (2) is unity, and finally the expression may be simplified to

$$\eta = 1.090 \times 10^{-8}\frac{M^{1/3}T^{1/2}}{V^{2/3}E_{vap}}e^{E_{vap}/nRT} \tag{3}$$

where M is the molecular weight, V is the molar volume, E_{vap} is the molar energy of vaporization, R is the gas constant for one mole, and n is a constant which may be considered as a "shape factor." Its value is approximately 3 for spherical molecules and 4 for elongated molecules. Equation (3) gives the viscosity of a liquid in terms of measurable quantities.

However, for higher values of $\frac{f\lambda^3}{2}$, that is, for high shearing stresses, the terms in the denominator of equation (2) cannot be neglected, and, as a result, the viscosity decreases with increasing shear, the condition for "non-Newtonian" flow.

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[4] H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936).

[5] R. H. Ewell and H. Eyring, *J. Chem. Phys.*, **5**, 726 (1937).

[6] R. H. Ewell, *J. Applied Phys.*, **9**, 252 (1938).

[7] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*. McGraw-Hill, New York, 1941, p. 477.

When one speaks of the "apparent viscosity" of a colloidal dispersion under a given set of conditions, one refers to the slope of the S curve (shown in Fig. 41) at a given pressure. The value of this "apparent viscosity" depends, in general, on the mechanical characteristics of the viscometer used for the measurement as well as on the pressure.

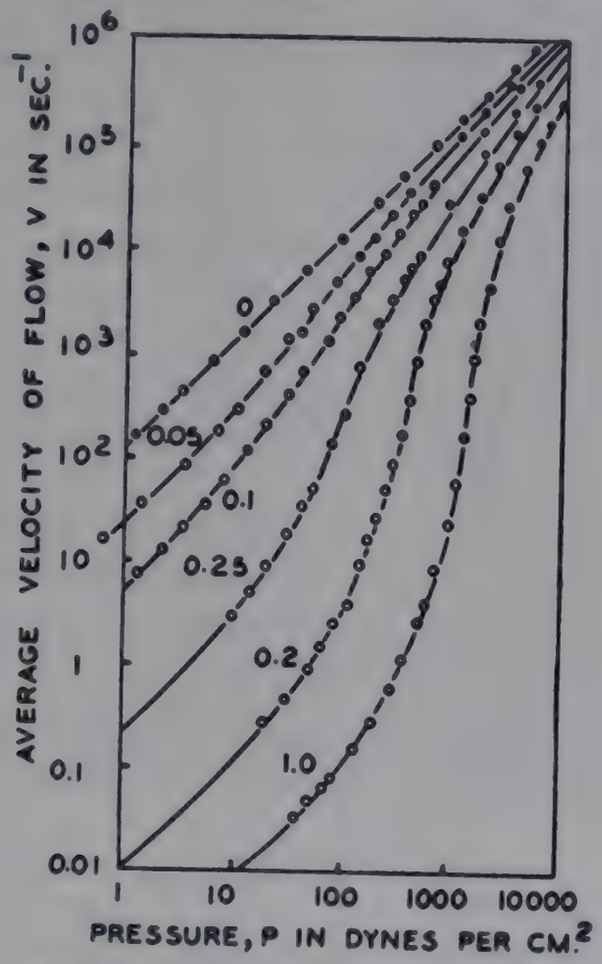

FIG. 42.—FLOW CURVES FOR VARIOUS CONCENTRATIONS OF CELLULOSE TRINITRATE (13.7% N) IN BUTYL ACETATE (PHILIPPOFF AND HESS[1]).

At very low and very high rates of shear, the S curve assumes an approximately constant slope corresponding to constant limiting values of apparent viscosity. Philippoff[8] designates the apparent viscosity at low shearing stresses as η_0, that at high shearing stressses as η_∞. He assumes that the apparent viscosity of a non-Newtonian liquid may be considered as the sum of a "real" viscosity and a "structural" part. Stated mathematically,

$$\eta_r = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + \frac{P^2}{\gamma^2}} \qquad (4)$$

[8] W. Philippoff, *Kolloid-Z.*, **71**, 1 (1935).

where η_r is the relative viscosity, defined as the ratio of the solution viscosity to the solvent viscosity, P is the pressure, and γ is a constant corresponding to a modulus of elasticity of the solution. In Figure 42 are a number of flow curves obtained by Philippoff and Hess[1] corresponding to several concentrations of nitrocellulose in butyl acetate. They show clearly the progressive increase of structure viscosity with concentration.

Most viscosity measurements on solutions of cellulose and its derivatives are made at very low pressures; hence, the quantity designated as η_0 is approximated. However, Conrad[9] has shown that, for cellulose of extremely high molecular weight in cuprammonium solution, η_0 cannot be evaluated precisely, either by extrapolating curves of apparent viscosity versus velocity gradient back to zero velocity gradient, or by means of equations developed for the purpose.[2, 10, 11] Hence, he favors converting all viscosity readings to values corresponding to a mean velocity gradient of 500 sec.$^{-1}$, since this value is easy to attain in ordinary capillary viscometers.

It has been suggested that the viscosity at high shearing stresses be considered in any evaluation of the characteristics of a cellulose product. Philippoff[12] uses the ratio η_∞/η_0 as a characteristic constant for the evaluation of structure viscosity. De Waele and Dinnis[13] use the ratio of two "mobilities," one of which is characteristic of shear at very low stresses and the other at high stresses. Mobility is defined as

$$M = \frac{dV'}{dS} \tag{5}$$

where V' = velocity gradient and S = stress. Since "mobility" is dimensionally equivalent to the reciprocal of viscosity, the latter ratio is equivalent to the reciprocal of Philippoff's ratio η_∞/η_0. De Waele and Dinnis point out that it is possible to prepare mixtures of high- and low-viscosity nitrocelluloses that have similar viscosities at low shearing stresses but very different viscosities at high shearing stresses. These facts indicate that, while viscosity measurements at low shearing stresses may provide information concerning solvent demand or ability of the colloid to disperse to a sol, measurements at high shearing stresses will provide information concerning the working properties of coating materials made from the

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[9] C. M. Conrad, *Ind. Eng. Chem., Anal. Ed.*, **13**, 526 (1941).
[10] R. V. Williamson, *Ind. Eng. Chem.*, **B21**, 1108 (1929).
[11] H. Staudinger and M. Sorkin, *Ber.*, **70B**, 1993, 2518 (1937).
[12] W. Philippoff, *Kolloid-Z.*, **75**, 155 (1936).
[13] A. de Waele and G. Dinnis, *Physics*, **7**, 426 (1936).

colloidal material. For example, high stress viscosity measurements on solutions of nitrocellulose should give considerable information regarding the spraying or brushing qualities of lacquers made from them, since the operations of spraying or brushing involve flow under relatively high shearing stresses.

In addition to approximate measurements of η_0 and η_∞, a numerical evaluation of structure viscosity may be obtained from graphs such as

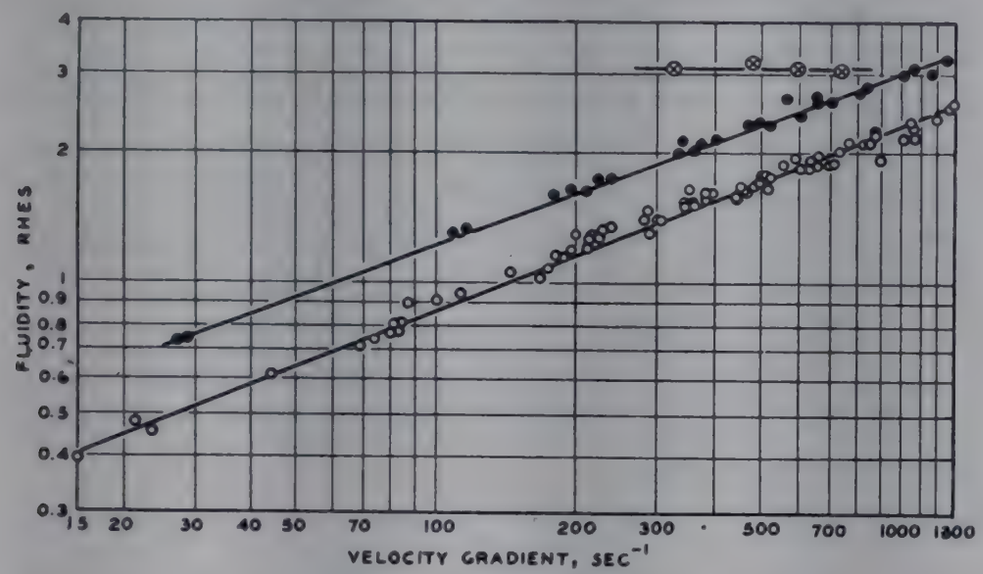

FIG. 43.—RELATION OF FLUIDITY OF 0.5% CUPRAMMONIUM SOLUTIONS OF COTTON CELLULOSE TO VELOCITY GRADIENT (CONRAD[9]).

●—Cotton cellulose, No. 1. ⊗—Approximately 71% aqueous
○—Cotton cellulose, No. 2. glycerol ("true" solution).

those presented by Conrad,[9] in which the relationship between fluidity (reciprocal of viscosity) and velocity gradient is plotted on a double-logarithmic scale. Figure 43 is an example of such a plot for cuprammonium solutions of two types of cotton cellulose, and for an aqueous solution of glycerol. The slopes of the straight-line functions are numerical constants associated with the structure viscosities of the solutions. For a "true" solution, the slope of such a curve is zero.

Another characteristic of structure viscosity is the fact that solutions having it exhibit the phenomenon of "relaxation" when stress is suddenly applied. This stress slowly decreases with time although the deformation remains the same. For a more complete treatment of this interesting phenomenon, a review by Gemant[14] should be consulted.

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[14] A. Gemant, *J. Applied Physics*, **13**, 210 (1942).

(*b*) *Effect of Concentration*

The effect of concentration on the viscosity of solutions of cellulose and its derivatives has been the subject of a great amount of study. The earlier work was primarily concerned with a means of converting the results of viscosity measurements made under different conditions to a common basis, in order to facilitate comparison. However, early attempts were also made to correlate solution viscosities with molecular weight. In this study, a characteristic constant related to molecular weight, derivable from viscosity measurements and independent of concentration and other variables, was sought. As a result of this search, the investigation of viscosity-concentration relationships assumed great importance.

The viscosities of solutions of cellulose and its derivatives, in common with those of other colloidal dispersions showing anomalous flow, increase very rapidly with increases in concentration. For very low viscosities and concentrations, this relationship is approximately linear. As the concentration increases, the curve gradually bends upward toward higher viscosities, and finally the viscosity becomes approximately proportional to the eighth power of the concentration.

Philippoff's Equation. Philippoff's equation,

$$\eta_r = \frac{\eta_{solution}}{\eta_{solvent}} = \left(1 + \frac{[\eta]C}{8}\right)^8 \tag{6}$$

seems to be one of the most generally applied of all the formulas heretofore proposed (see Section E of this chapter). Furthermore, it contains but one "characteristic" constant: $[\eta]$. For low viscosities, this equation becomes

$$\eta_r = 1 + [\eta]C \quad \text{(From a power series development)}$$

or

$$\eta_{sp} = [\eta]C \tag{7}$$

where $\eta_{sp} = \eta_r - 1$. In this form, $[\eta]$ is seen to be equivalent to the product $K_M M = \frac{\eta_{sp}}{C}$ (a characteristic constant) in Staudinger's molecular-weight equation (see equation (29) in Section E of this chapter), the difference being in the units in which concentrations are expressed in the two cases. The factor $[\eta]$ is also equivalent to Kraemer and Lansing's "intrinsic viscosity"[15] which they defined as

$$[\eta] = \lim_{C \to 0} \left(\frac{\eta_{sp}}{C}\right)$$

[15] E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 153 (1935).

For a number of different systems, the Philippoff equation is valid over a wide range of concentrations. A typical case illustrating the use of the Philippoff equation is the following: A sample of nitrocellulose is dissolved in butyl acetate in unit concentration. Its relative viscosity is measured, and the values for η_r and C are substituted in the Philippoff equation. $[\eta]$ is computed, and serves as a basis of comparison between solutions of this sample in both low and high concentrations.

The importance of determining the intrinsic viscosity with considerable accuracy should not be underestimated, inasmuch as, at concentrations near zero, the state of a truly viscous solution is most closely approached, and quantities characteristic of the substance being investigated can be evaluated without complications arising from the multitude of variables found at high concentrations. Hence, any mathematical aid to the accurate evaluation of these characteristic quantities is a boon to the investigator. These factors account for the large amount of work which has been done on the problem.

Kauppi and Bass[16] have determined the viscosity-concentration relations for ethylcellulose solutions. In order to present their data in a form convenient to the lacquer trade, they have converted Philippoff's equation into an expression giving the relationship between solution viscosity and concentration, instead of that between relative viscosity and concentration. From Philippoff's[1] equation (see equation (6) above)

$$\eta_{solution} = \eta_{solvent}\left(1 + \frac{[\eta]C}{8}\right)^8$$

or

$$\sqrt[8]{\eta_{solution}} = \sqrt[8]{\eta_{solvent}}\left(1 + \frac{[\eta]C}{8}\right)$$

or

$$\sqrt[8]{\eta_{solution}} = k' + KC$$

where

$$k' = \sqrt[8]{\eta_{solvent}} \text{ and } K = \frac{k'[\eta]}{8}$$

It is seen that, when the eighth root of the solution viscosity is plotted against concentration, a straight line should result. From the curves of Figure 44, taken from the work of Kauppi and Bass,[16] which are plotted in the foregoing manner, it will be seen that ethylcellulose obeys Philippoff's law in concentrations above 5%. Below that concentration, there is a

[16] T. A. Kauppi and S. L. Bass, *Ind. Eng. Chem.*, 29, 800 (1937).

break in the line, and, near zero concentration, the line becomes a curve. Viscosity measurements up to 25% concentration on the ethylcellulose sample represented by Curve 4 result in values which are still on the straight-line portion.

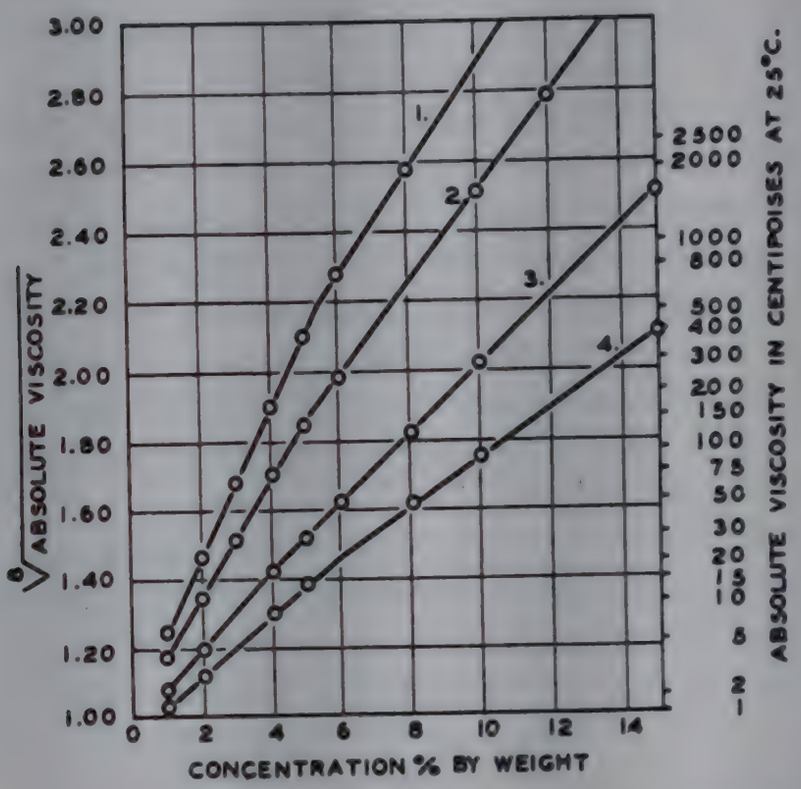

FIG. 44.—VISCOSITY-CONCENTRATION CURVES OF ETHYLCELLULOSE IN 80:20 TOLUENE-ETHANOL (KAUPPI AND BASS[16]).

Absolute viscosity of 5% solution

1. 381 cps.
2. 134 cps.
3. 30 cps.
4. 13 cps.

From the type of data represented by Figure 44, the chart of Figure 45 was prepared. If the viscosity of an ethylcellulose at one concentration is known, the viscosity at any other concentration in the same solvent may be found from Figure 45. If the effects of temperature and solvent are known at any one concentration, Figure 45 may still be used to determine the effects caused by the same change at another concentration. This is a direct result of the fact, first pointed out by Philippoff, that any means of changing the viscosity (change in solute, solvent, or temperature) changes only the position of the straight line (the value of the $[\eta]$) expressing the relation between the eighth root of the viscosity and the concentration and not the straight-line relationship itself. In other words, the equation, with its appropriate $[\eta]$, is valid in each case.

The foregoing graphical method is generally applicable to solutions of all other cellulose compounds and of other linear polymers which obey Philippoff's equation.

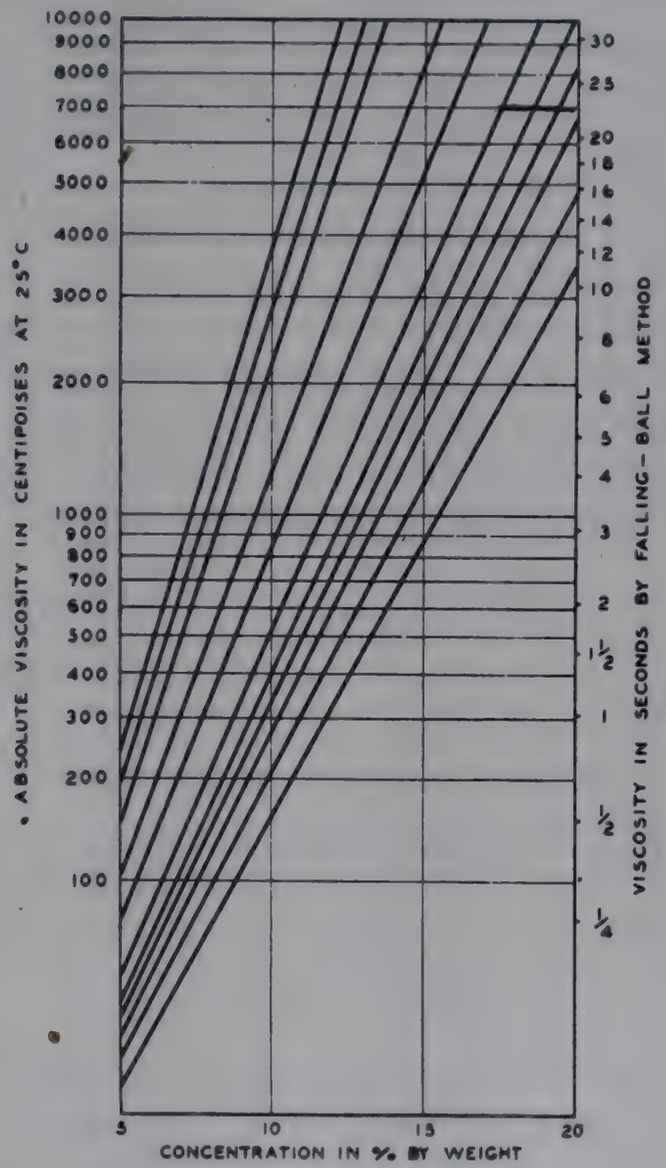

FIG. 45.—ETHYLCELLULOSE VISCOSITY-CONCENTRATION CHART (KAUPPI AND BASS[16]).

Takei and Erbring[17] found that the viscosities of cellulose acetates in various solvents obey a modified Philippoff equation:

$$\eta_r = \left(1 + \frac{[\eta]'}{8} C\right)^8 \text{ where } [\eta]' = \frac{1}{aC + \frac{1}{k}} \qquad (8)$$

a and k being constants. Previous studies of the dielectric properties of the same cellulose acetate solutions showed that there was neither appre-

[17] M. Takei and H. Erbring, *Kolloid-Z.*, 95, 207 (1941).

ciable association between chains nor variation in the degree of solvation within the concentration range studied. An interesting correlation between the constant a of the modified Philippoff equation and the quantity $\mu^2/\epsilon\sigma$ (where μ = the dipole moment, ϵ = the dielectric constant, and σ = the surface tension) was found. High values of a are associated with low values of $\mu^2/\epsilon\sigma$. However, only limited experimental evidence is available, so too much importance should not be attached to this correlation.

Martin's Equation. Martin,[18] investigating cuprammonium solutions of cellulose, found that none of the various viscosity-concentration equations were sufficiently accurate for this material. He developed, by empirical means, an equation which was found to hold within experimental error, not only for cuprammonium solutions of cellulose, but also for solutions in various solvents of nitrocellulose, cellulose acetate, ethylcellulose, polystyrene, poly-ω-hydroxydecanoic acid, rubber, gelatin, and phenol-formaldehyde condensation products. This equation is

$$\frac{\eta_{sp}}{C} = [\eta]e^{k'[\eta]C} \quad \text{or} \quad \log \frac{\eta_{sp}}{C} = \log [\eta] + K[\eta]C \tag{9}$$

where $K = k'/2.3$.

Equation (9) represents a series of straight lines on a plot of $\log \frac{\eta_{sp}}{C}$ against concentration. This equation is similar to one proposed by Staudinger,[19]

$$\log \frac{\eta_{sp}}{C} = \log [\eta] + K_{st}C \tag{10}$$

where K_{st} was called by Staudinger the *Steigungskonstante*, and is the slope of the line representing the equation. Staudinger found that calculated values of his *Steigungskonstante* were linearly related to molecular weights in the case of polystyrene. This relationship was

$$K_{st} = K_{mst}\mathrm{M} + b \tag{11}$$

where K_{mst} and b are constants. Due to the appearance of the second constant b, a simple relationship cannot be developed by substituting equation (11) in equation (10). Martin, however, by introducing the intrinsic viscosity $[\eta]$ into the concentration term, was able to eliminate this second constant because of the fact that the curve of K_{st} versus $[\eta]$ passed

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[18] A. F. Martin, Am. Chem. Soc. meeting, Memphis, April 20–24, 1942.

[19] H. Staudinger and W. Heuer, *Z. physik. Chem.*, **A171**, 129 (1934).

through the origin for every system of high-molecular-weight compounds which he studied.

Martin's equation is accurate only for concentrations below 5%. In

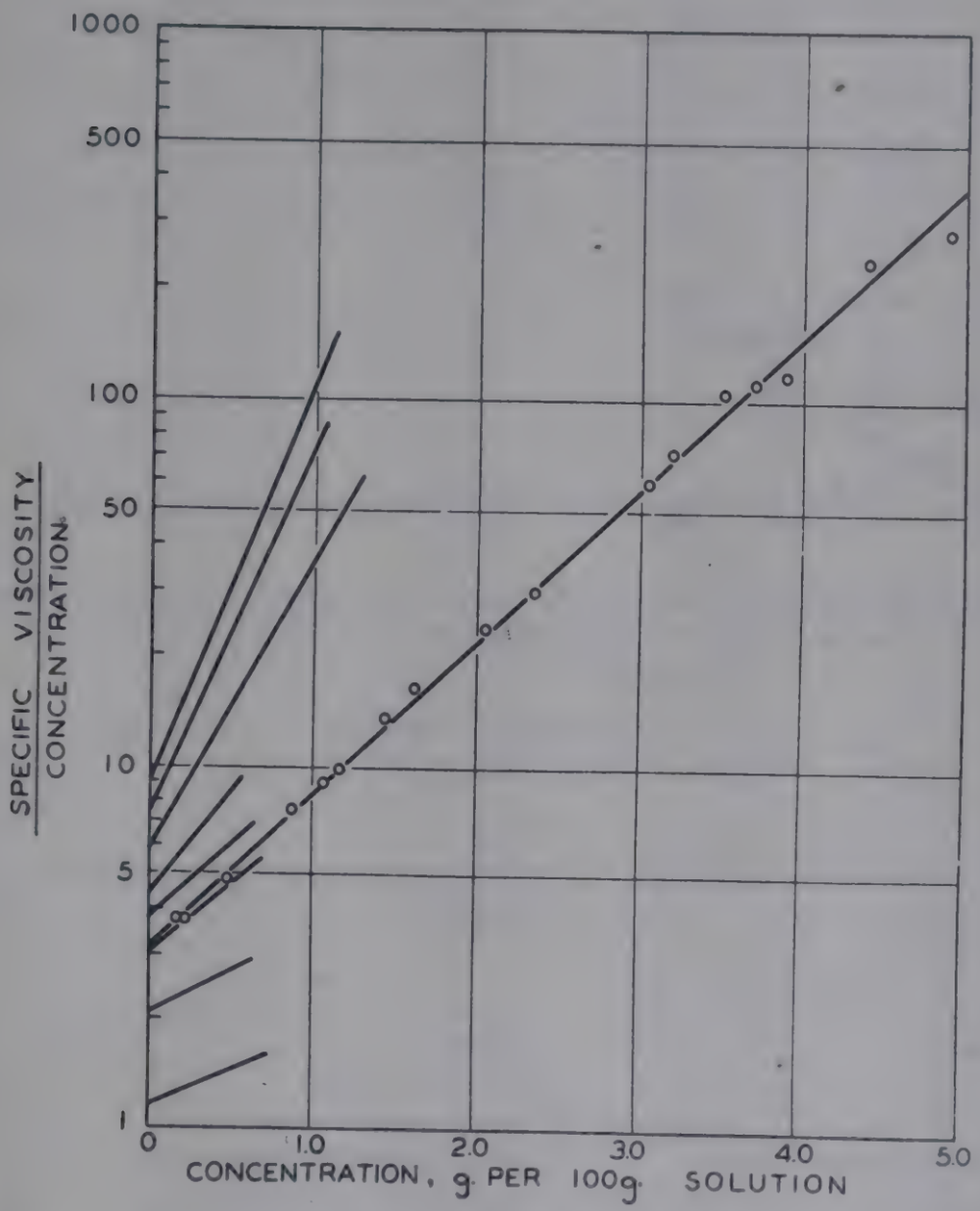

FIG. 46.—VISCOSITY-CONCENTRATION RELATIONSHIPS FOR CELLULOSE IN CUPRAMMONIUM HYDROXIDE (MARTIN[18]).

Curve with experimental points represents only solution which was measured in concentrations above 1%.

Figure 46 is plotted log $\frac{\eta_{sp}}{C}$ versus C for several solutions of cellulose in cuprammonium hydroxide. The slopes of these lines are equal to $K[\eta] = K_{st}$. These slopes are plotted against corresponding values of $[\eta]$ deter

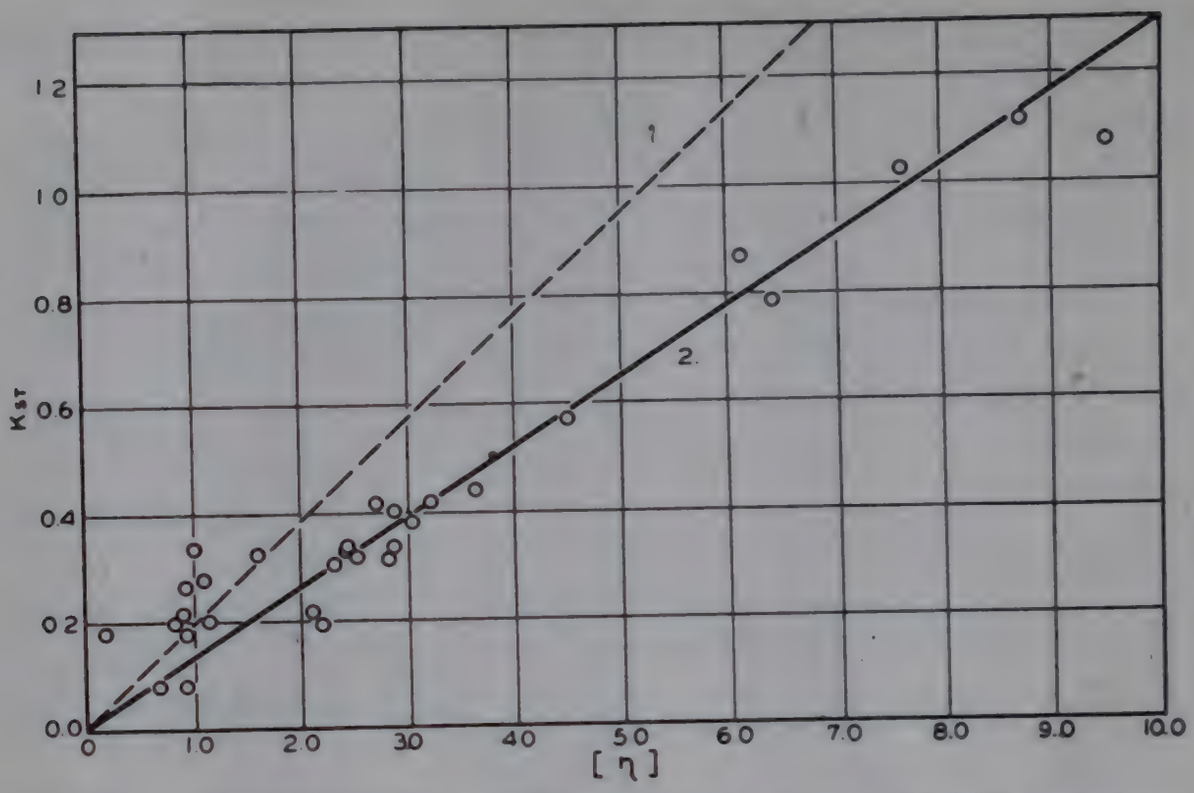

FIG. 47.—*Steigungskonstante* (SLOPE CONSTANT) VERSUS INTRINSIC VISCOSITY FOR CELLULOSE IN CUPRAMMONIUM HYDROXIDE (MARTIN[18]).

Curves:

1. Philippoff's equation.
2. K = slope = 0.130.

TABLE 1

VALUES OF MARTIN'S CONSTANT (K) FOR SOLUTIONS OF SEVERAL HIGH POLYMERS (MARTIN[18])

Solute	Solvent	$K = \frac{k'}{2.3}$
Polystyrene	Tetralin	0.056
	Benzene, toluene	0.102
	Methyl ethyl ketone	0.216
Poly-ω-hydroxydecanoic acid	*sym*-Tetrachloroethane	0.100
Cellulose	Cuprammonium hydroxide	0.130
Ethylcellulose	80:20 Toluene-ethanol	0.111
Gelatin	Water	0.14
Rubber	Chlorobenzene	0.158
Cellulose acetate	*sym*-Tetrachloroethane	0.150
	Acetone	0.178
	Methyl Cellosolve	0.178
	Chloroform	0.178
Nitrocellulose	Butyl acetate	0.180
	Cellosolve	0.200
	Acetone	0.247
Phenol-formaldehyde resin	Acetone	0.57

TABLE 2

EQUATIONS RELATING VISCOSITY AND CONCENTRATION (MARTIN[18])

Curves in Figure 48	Investigator	General equation	Value of constants for cellulose in cuprammonium hydroxide $[\eta] = 1.0$
1, 10	Martin[18]	$\log (\eta_{sp}/C) = \log [\eta] + K[\eta]C$	$K = 0.130$
2, 6	Philippoff[1]	$\eta_r = (1 + \frac{[\eta]}{8} C)^8$	.....
3, 12	Baker[20]	$\eta_r = (1 + aC_v)^K$	$a = \frac{[\eta]}{K}$; $K = 3.6$
4	Farrow, Neale[21]	$1 + K/C = B/\log \eta_r$	$B = 11$; $K = 25.3$
5	Arrhenius[22]	$\log \eta_r = KC_v$	$K = 0.4343$
7	Bredée, de Booys[23]	$\eta_r = \left(1 + \frac{2.5V_0}{6} C_v\right)^6$	$2.5\ V_0 = [\eta]$
8	Fikentscher[24]	$\log \eta_r = \left(\frac{75K^2}{1 + 1.5KC_v} + K\right)C_v$	$K = 0.0697$
9	Fikentscher, Mark[25]	$\eta_r = 1 + K \frac{bC_v}{1 - bC_v}$	$Kb = 1$; $b = 0.1552$
9	Schulz, Blaschke[26]	$\eta_{sp}/C = [\eta](1 + K\eta_{sp})$	$K = 0.1552$
11	Papkov* [27]	$\log \eta_r = KC_v^a$	$K = 0.325$; $a = 0.892$
12	Takei, Erbring[17]	$\eta_r = \left(1 + \frac{[\eta]C}{8(1 + ac[\eta])}\right)^8$	$a = 0.468$
13	Bredée, de Booys[28]	$\log \eta_r = K'C(1 + C + 0.1K'C)^{A-1}$	$K' = \frac{1}{2.3}$; $A = 0.744$

* Because of the form of this equation, no finite values of $[\eta]$ can be obtained unless $a = 1.0$, in which case the equation is identical with the Arrhenius equation (5). The values of K and a given above were chosen so the curve passed through the experimental point at $C = 5$ and through an arbitrary point at $\eta_{sp}/C = 1.05$, $C = 0.1$.

[20] F. Baker, *J. Chem. Soc.*, **103,** 1653 (1913). [21] F. D. Farrow and S. M. Neale, *J. Textile Inst.*, **15,** T157 (1924). [22] S. Arrhenius, *Z. physik Chem.*, **1,** 286 (1887). [23] H. L. Bredée and J. de Booys, *Kolloid-Z.*, **79,** 31 (1937). [24] H. Fikentscher, *Cellulosechem.*, **13,** 58 (1932). [25] H. Fikentscher and H. Mark, *Kolloid-Z.*, **49,** 135 (1929). [26] G. V. Schulz and F. Blaschke, *J. prakt. Chem.*, **158,** 130 (1941). [27] S. Papkov, *Kunststoffe*, **25,** 253 (1935). [28] H. L. Bredée and J. de Booys, *Kolloid-Z.*, **91,** 39 (1940).

mined from the intercepts on the log $\frac{\eta_{sp}}{C}$ axis at zero concentration. A straight line passing through the origin results (Fig. 47). The slope of this line is equal to the K in Martin's equation and is a characteristic quantity for a given system; for example, cellulose in cuprammonium hydroxide has a K value of 0.130. K varies with solvent and solute but is the same for

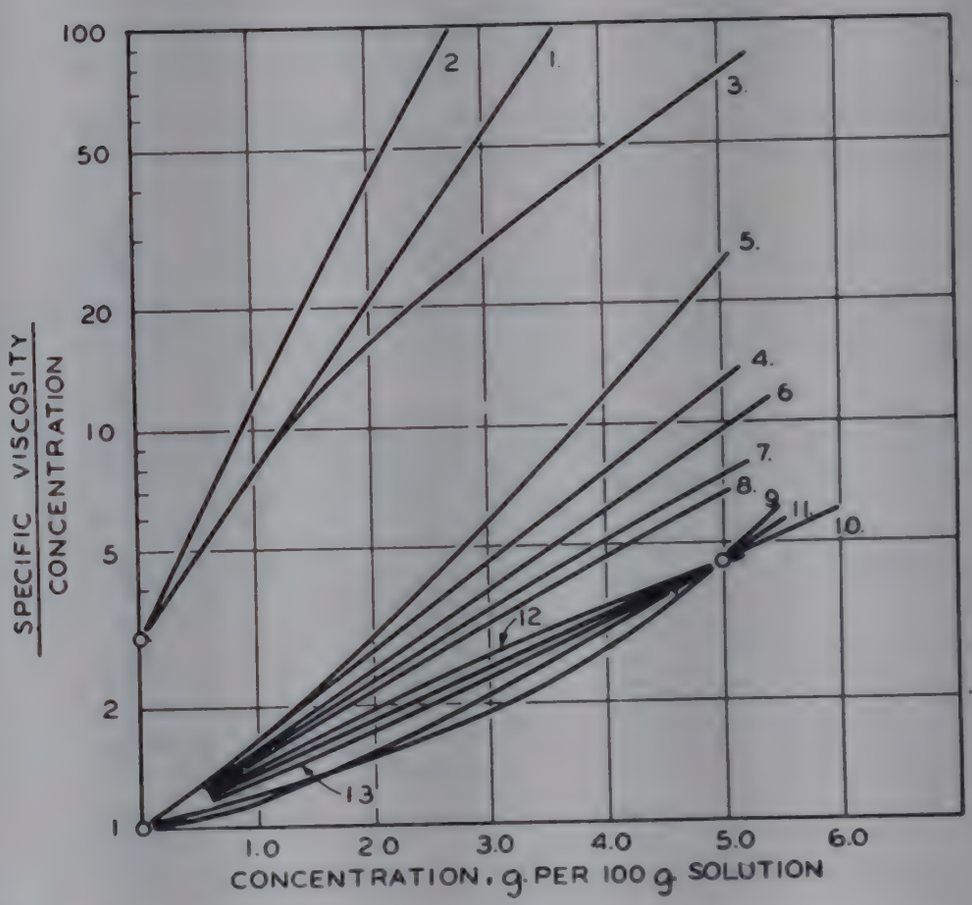

FIG. 48.—COMPARISON OF EQUATIONS RELATING VISCOSITY AND CONCENTRATION (MARTIN[18]).

Experimental data for cellulose in cuprammonium hydroxide are represented by Curves 1 and 10.

members of a given polyhomologous series dissolved in a single solvent. It is a dimensionless quantity and, hence, is independent of the manner in which solute concentration is expressed. Its temperature variation appears to be very small for all the systems examined. Values of K for other high polymers are listed in Table 1. A mathematical analysis of Philippoff's equation shows that it will satisfactorily represent only those systems which have K values close to 0.19. Certain solutions of cellulose acetate and

nitrocellulose fall in this class, but cuprammonium solutions of cellulose do not, as may be seen by an examination of Figure 47 and Table 1.

Table 2 lists a number of the more familiar viscosity-concentration equations. Figure 48 is a graphical comparison of these equations as applied to solutions of cellulose in cuprammonium hydroxide. Curves 1 and 10 of Figure 48 represent experimental data on cuprammonium solutions of two samples of cellulose. Corresponding plots of Martin's equation, which agree closely with the experimental data, are also represented by Curves 1 and 10.

In Section E of this chapter, the correspondence between Martin's equation and the theoretically derived Huggins' equation was shown, together with the limitations of each.

Martin's equation appears from the foregoing considerations to be the most useful of the ones discussed for obtaining intrinsic viscosities for molecular-weight calculations from the formulas of Kraemer[29] and Staudinger.[30] Kraemer's equation is

$$\text{Degree of Polymerization (D.P.)} = k[\eta] \tag{12}$$

where k is a constant. Staudinger's equation is usually written

$$[\eta] = K_M M \tag{13}$$

(c) *Effect of Solvent*

It appears to be a well-established fact that the solution viscosities of cellulose and cellulose derivatives (in common with those of other high polymers) are due in part, at least, to the presence of solvate layers. The true nature of this phenomenon is not yet known; hence, much of the work done in this field is highly qualitative and empirical. (See, however, the discussion of this subject in Section E of this chapter.)

Cochrane and Leeper[31] have investigated the effect of various solvents and solvent mixtures on the viscosities of 5% solutions of nitrocellulose. It was found that additions of alcohol up to 40–60% to solutions of nitrocellulose in mixtures of ethyl acetate and ethyl alcohol or butyl acetate and ethyl alcohol reduce the viscosity of the solution, while beyond this point the viscosity rises. Butyl alcohol has the same effect as ethyl al-

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[29] E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

[30] H. Staudinger, *Die hochmolekularen organischen Verbindungen.* J. Springer, Berlin, 1932, p. 52 *et seq.*

[31] J. R. Cochrane and G. W. Leeper, *J. Soc. Chem. Ind.*, **46**, T117 (1927).

cohol. For mixtures of ethyl acetate and butyl acetate, the viscosity corresponding to a given concentration may be obtained from the straight line connecting the points corresponding to the pure esters. Benzene be-

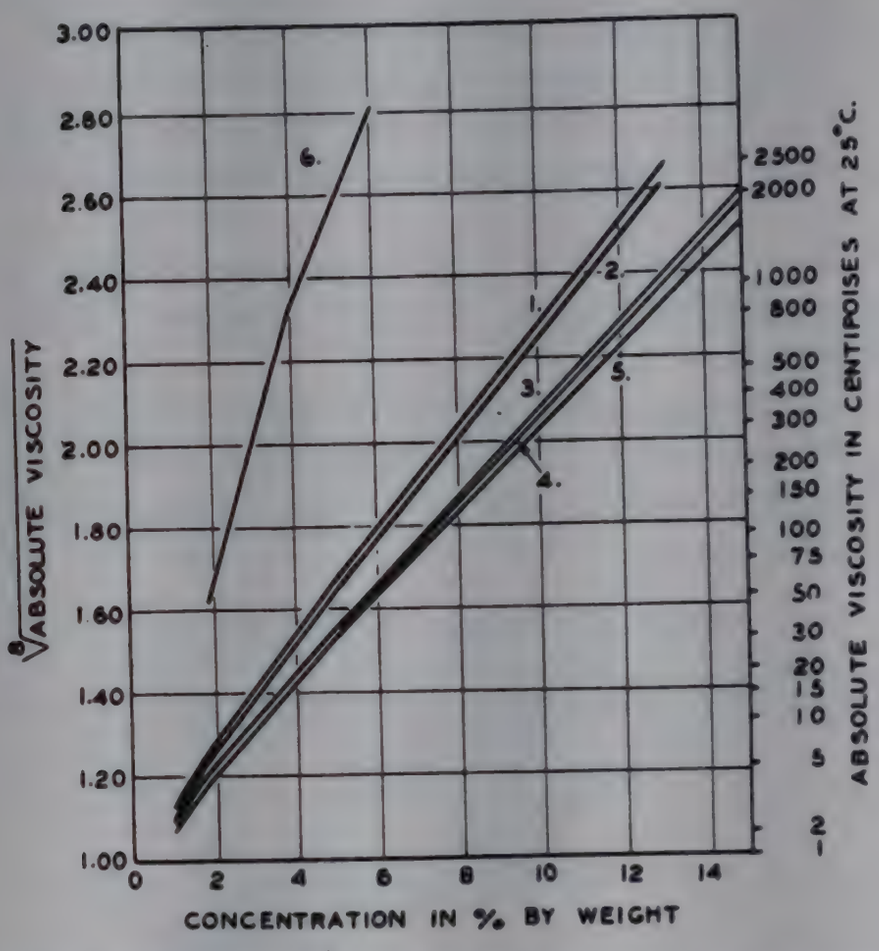

FIG. 49.—EFFECT OF SOLVENT ON VISCOSITY-CONCENTRATION CURVES OF ETHYLCELLULOSE (KAUPPI AND BASS[16]).

Curve	Solvent
1	Toluene 20, butyl acetate 80
2	Xylene 70, butanol 30
3	Butyl acetate 60, ethanol 40
4	Toluene 80, ethanol 20
5	Toluene 70, ethanol 30
6	Toluene

haves as a diluent when mixed with the pure esters, but, in the presence of alcohol, it has marked solvent properties.

Kauppi and Bass[16] have shown the effect of change of solvent on solutions of ethylcellulose. In Figure 49, the eighth root of the solution viscosity is plotted against concentration for solutions of a 30-centipoise ethylcellulose in toluene, 20:80 toluene-butyl acetate, 70:30 xylene-butanol, 60:40 butyl acetate-ethanol, 80:20 toluene-ethanol, and

70:30 toluene-ethanol. These results confirm Philippoff's observation that the effect of a change in solvent is merely to change the value of $[\eta]$ in his equation.

McBain, Harvey, and Smith,[32] and McBain, Grant, and Smith[33] found that the ability of a solvent to dissolve nitrocellulose could be measured by the viscosity of the resulting solution, with the best solvents giving the least viscous solutions. They also found that mixtures appeared to be better solvents than their pure constituents. Solvent power was measured by these workers as the average slope of the curve representing the relationship between the logarithm of the relative viscosity and the concentration.

Danilov and Aleksandrova[34] have investigated the viscosity of solutions of ethylcellulose in a number of solvents and solvent mixtures. They find that ethylcellulose solutions, unlike those of cellulose acetate, are unaffected by the dipole moments of the solvents used.

Rocha[35] and Suida[36] have examined the viscosity relationships in the system cellulose acetate–acetone–water.

(*d*) *Effect of Temperature*

A number of investigators have examined the effect of temperature on the viscosities of solutions of cellulose and its derivatives. For example, Clibbens and Geake[37] early showed the dependence of viscosity on temperature in the case of cuprammonium solutions of cellulose. Their data showed a decrease in viscosity with increasing temperatures for this system. Shinoda and Inagaki[38] have found a temperature effect in the case of cellulose acetate in various solvents which could be expressed by a relationship of the type

$$\eta = Ae^{-Bt} \tag{14}$$

where A and B are constants, and t is the temperature. Hirata and Daimon[39] found the same relationship to hold for concentrated solutions (22.88%) of nitrocellulose in acetone in the range from 8 to 40°C.

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[32] J. W. McBain, C. E. Harvey, and L. E. Smith, *J. Phys. Chem.*, **30**, 312 (1926).
[33] J. W. McBain, E. M. Grant, and L. E. Smith, *J. Phys. Chem.*, **38**, 1217 (1934).
[34] S. N. Danilov and R. S. Aleksandrova, *Narodnuiĭ Komissariat Tyazheloĭ Prom. S.S.S.R., Leningrad Plastmassui*, **1**, 100 (1935).
[35] H. J. Rocha, *Kolloid-Beihefte*, **30**, 230 (1930).
[36] H. Suida, *Cellulosechem.*, **12**, 310 (1931).
[37] D. A. Clibbens and A. Geake, *J. Textile Inst.*, **19**, T77 (1928).
[38] R. Shinoda and E. Inagaki, *Cellulose Ind.* (Tokyo), **12**, 221 (1936).
[39] F. Hirata and T. Daimon, *J. Soc. Chem. Ind., (Japan)*, **37**, B459 (1934).

Karrer, Berl, and Umstätter[40] have presented a large amount of data on the viscosity-temperature relationships of cellulose acetate and nitrocellulose in various solvents. They found that their data fit an equation of the type

$$\log \frac{1}{\eta} = A - \frac{Q}{RT} \tag{15}$$

where A, Q, and R are constants, and T is the absolute temperature.

Philippoff[1, 2] has tested the validity of his equation over a range of temperatures and has found that only the value of the intrinsic viscosity $[\eta]$ is altered. Kauppi and Bass[16] have verified these observations in the case of ethylcellulose solutions. When the temperature changes, the effect on the viscosity-concentration curve is to shift it along the concentration axis. Philippoff and Hess[1] have found a linear relationship between intrinsic viscosity and temperature of the form

$$[\eta] = \frac{A}{T + T_0} \tag{16}$$

where A and T_0 are constants, and T is the absolute temperature.

Eyring's equation (equation (2)) predicts the variation of viscosity with temperature. For low shearing stresses it may be shown that the theoretical equation reduces to the form

$$\eta = Ae^{B/T} \tag{17}$$

This linear relationship between the logarithm of the viscosity and the reciprocal of the temperature has been confirmed experimentally for many liquids. It agrees in form with that presented by Karrer, Berl, and Umstätter.[40]

(e) *Viscosity of Mixtures*

Philippoff[2] has derived a blending equation for the determination of the viscosities of mixtures from the viscosities and concentrations of the constituents:

$$C_0[\eta]_0 = \Sigma C_i[\eta]_i \tag{18}$$

where C_0 is the total concentration of the mixture, $[\eta]_0$ is the intrinsic viscosity of the mixture, C_i is the concentration of each individual constituent, and $[\eta]_i$ is the intrinsic viscosity of each constituent.

Kauppi and Bass[16] have constructed a blending chart by plotting the percentage of one component in a mixture of two samples of ethylcellulose

[40] E. Karrer, E. Berl, and H. Umstätter, *Kolloid-Beihefte*, **34**, 22 (1932).

against the eighth root of solution viscosity in 5% solution with 80:20 toluene-ethanol. Figure 50 shows this chart. A line is drawn between the viscosities of the two components, and the percentage of the right-hand component corresponding to the viscosity desired is read. This type of blending chart has been used for mixtures of ethylcelluloses and nitrocelluloses as well as for ethylcelluloses alone. These charts are accurate over a considerable range of viscosity differences.

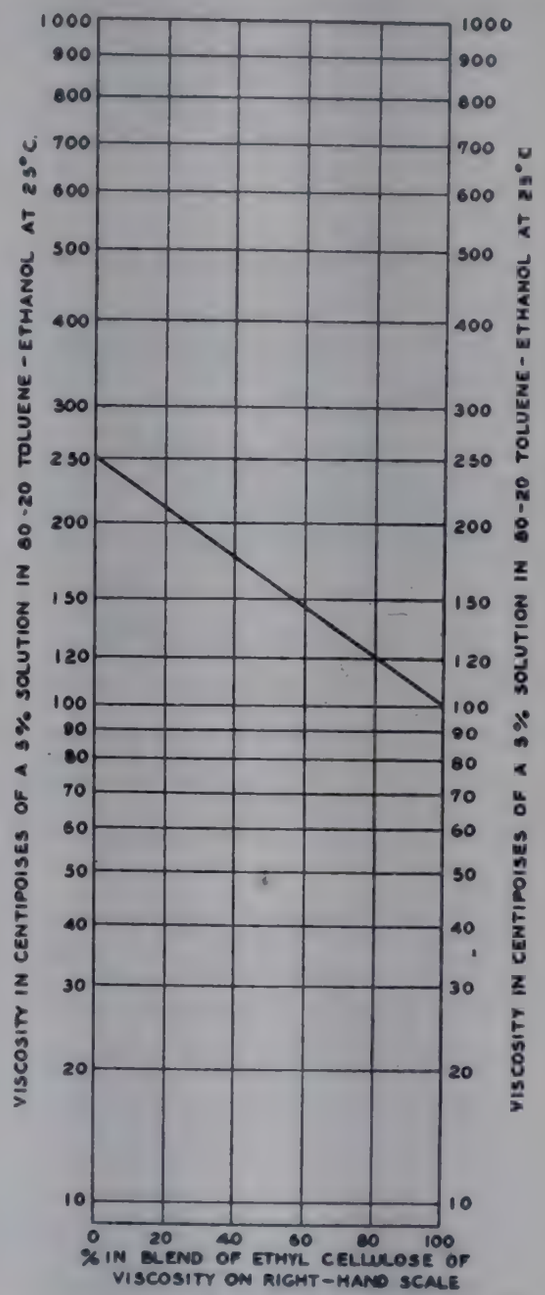

FIG. 50.—ETHYLCELLULOSE BLENDING CHART (KAUPPI AND BASS[16]).

(f) *Fractionation of Nitrocellulose*

Lipatova and Lipatov[41] have separated nitrocellulose into four fractions by gradual precipitation with water. Those fractions which had high viscosities in nitrobenzene solution were found also to have high temperature coefficients of viscosity. The authors found that the ratio of viscosities of two fractions in various solvents (for example, nitrobenzene, acetone, benzene, and methanol) is not constant.

2. Measurement of Viscosity

(a) *Theory of Measurement*

The fundamental principles forming the basis for the most commonly used types of viscometers are derived from Newton's equation (equation (1)). For example, in the case of steady flow through a straight tube of uniform cross section, Newton's equation takes the form

$$S = \eta \frac{dv}{dr} \qquad (1a)$$

where S is the shearing stress, η is the coefficient of viscous flow, v is the

[41] G. V. Lipatova and S. M. Lipatov, *Colloid J.*, (*U.S.S.R.*), **5**, 647 (1939).

velocity directed along the axis of the tube, and r is the radial distance measured outward from the axis of the tube.

Steady Flow of Liquid through a Cylinder. Integration[42] of this equation gives for the total liquid flux across any section of the tube (that is, the total volume of liquid flowing through the tube in unit time)

$$F = \frac{\pi \Delta p}{8\eta l} a^4 \tag{19}$$

where a is the radius of the tube, l is its length, and Δp is the pressure differential at the ends of the tube. This equation, given here as an integration of Newton's equation, was first established empirically by Poiseuille, and bears his name.

The coefficient of viscosity η is defined in the c.g.s. system in such a manner that the flux F is the total volume of liquid in cubic centimeters flowing through the tube per second, Δp is measured in dynes per square centimeter, l and a in centimeters. Under these conditions, η is expressed in poises. Its dimensions are $ML^{-1}T^{-1}$ We see, then, that a poise may be defined as the pressure differential in dynes per square centimeter required to maintain a flow of 1 cc. per second through a tube 1 cm. in radius and 1 cm. long. Alternative definitions will, of course, follow from equations (1a) and (19). The viscosity of water at 20°C. is approximately one centipoise.[43]

Refined viscosity measurements by the capillary-tube method involve a number of corrections, one of the most important of which is due to the fact that only a portion of the pressure differential Δp in equation (19) is caused by the viscous resistance of the liquid. The remainder is due to the velocity of liquid in the tube, according to the well-known theorem of Bernoulli. Because it is necessary to consider the kinetic energy of the system in order to evaluate the Δp due to viscous resistance, the correction which must be applied to equation (19) is known as a kinetic energy correction. This takes the form

$$\Delta p' = \Delta p - \frac{\rho Q^2}{\pi a^4} \tag{20}$$

where $\Delta p'$ is the pressure differential caused by the viscous resistance alone, ρ is the density of the liquid, Q is the total volume flowing through the tube in unit time, and a is the radius of the tube.

Poiseuille's law was developed on the basis of flow through a cylindrical

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[42] H. Lamb, *Hydrodynamics*. 6th ed., University Press, Cambridge, 1932. p 585 *et seq.*

[43] 1.0087 centipoises according to the *International Critical Tables*, Vol. V, p. 10.

tube. Obviously, the treatment can be generalized to include all types of flow. However, for the sake of definiteness, only two others will be considered here. They are the type associated with a falling sphere, and a special case of flow between concentric cylinders.

Sphere Falling through a Liquid. Stokes' law[42] for the velocity with which a sphere moves through a viscous medium under the influence of gravity alone is

$$\eta = \frac{2}{9}\frac{gr^2(D-d)t}{S} \tag{21}$$

where g is the acceleration of gravity, r is the radius of the sphere, D is the density of the sphere, d is the density of the liquid, t is the time of fall of the sphere, and S is the height of fall.

More accurate formulas for computing viscosities by the falling-sphere method are modifications of Stokes' law. Equation (22) is the Francis[44] modification:

$$\eta = \frac{2}{9}\frac{gr^2(D-d)t}{S}\left[1-\frac{r}{R}\right]^{2.25} \tag{22}$$

where R is the radius of the containing cylinder.

The Ladenburg[45] modification is

$$\eta = \frac{2}{9}\frac{gr^2(D-d)t}{S\left(1+2.4\frac{r}{R}\right)\left(1+3.3\frac{r}{H}\right)} \tag{23}$$

where H is the total height of the liquid.

An equation due to Faxén[46] is

$$\eta = \frac{2}{9}\frac{gr^2(D-d)t}{S}\left[1-2.104\left(\frac{r}{R}\right)+2.09\left(\frac{r}{R}\right)^3-0.95\left(\frac{r}{R}\right)^5\right] \tag{24}$$

Equation (24) is the most accurate of the three modifications.

Rotation of Concentric Cylinders in a Liquid. For the case[42] of two cylinders of radii a and b and of infinite length, one of which is stationary and the other moving, with a liquid of viscosity η between them, the turning moment per unit length M required to produce an angular velocity ω is,

$$M = 4\pi\eta\omega\frac{a^2b^2}{b^2-a^2} \tag{25}$$

The three cases of flow considered in the foregoing discussion are the

[44] A. W. Francis, *Physics*, **4**, 403 (1933).

[45] R. Ladenburg, *Ann. Physik*, [4], **20**, 287 (1907); [4], **23**, 447 (1907).

[46] H. Faxén, Dissertation, Upsala, 1921; *Ann. Physik*, **68**, 8 (1922); *Arkiv Mat., Astron. Fysik*, **17**, No. 27 (1922).

bases for the three most common types of instruments for measuring viscosity; namely, the capillary types, the falling-ball viscometers, and the concentric-cylinder types. Examples of such instruments will be described below.

In equations (1a) and (19) to (25), inclusive, the coefficient of viscosity η has been defined as a constant. The reader should recall that these equations were established for ordinary or Newtonian solutions, meaning those solutions having viscosities which are independent of shearing stress. If the viscometers are properly designed to avoid disturbing effects such as turbulence, the type used does not affect the results obtained for such solutions.

(*b*) *Measuring Instruments*

For convenience, viscometers now in use may be classified into five general groups.

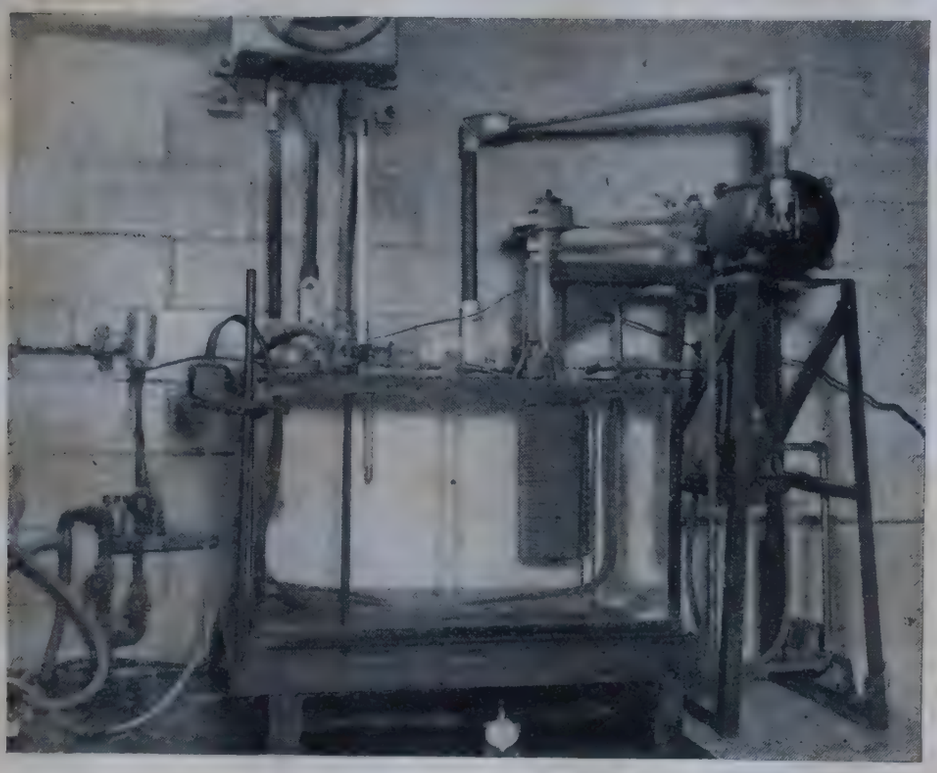
1. The falling-ball type.
2. Rotational type.
3. Capillary-tube type.
4. Short-tube or efflux-type.
5. Miscellaneous types.

Falling-Ball Viscometer. The falling-ball method is normally used only for liquids of high viscosity. These invariably have high temperature coefficients, and it is, therefore, necessary to have accurate temperature regulation while making measurements. In order to obtain consistent results, it is also necessary that the balls be of uniform diameter, and that suitable provision be made for each ball to drop down the center of the containing tube, because the side walls of the tube have a marked effect on the fall of the ball. The ratio of the radius of the cylinder to that of the ball should be sufficiently large so that the effect of the side walls will be small. However, this factor is not critical where relative measurements are being made. One of the principal disadvantages of the falling-ball method is the relatively large volume of liquid required for each test. The advantages are its simplicity, ruggedness, and relatively low cost.

The standard method of the American Chemical Society[47] for the determination of the viscosity of cuprammonium solutions of cellulose calls for a glass sphere 0.125 in. (3.175 mm.) in diameter having a specific gravity ranging between 2.4 and 2.6. This sphere, falling through the cupram-

[47] E. K. Carver and Committee, *Ind. Eng. Chem., Anal. Ed.*, **1**, 49 (1929).

monium solution contained in a glass tube 30 cm. long and 1.4 cm. inside diameter, is timed through the middle 15 cm. of the tube. The viscosity, being directly proportional to the time of fall, is expressed in seconds. With this apparatus, each second of fall corresponds to 22.3 centipoises.



Courtesy of Hercules Powder Company

FIG. 51.—HERCULES FALLING-BALL VISCOMETER.

This photograph shows the steel ball falling through the viscous medium which is contained in a glass tube (1 in. in diameter). The tube is surrounded by a constant-temperature bath fitted with a motor-driven stirrer.

The falling-ball method used by the Hercules Powder Company for specifying viscosity types of nitrocellulose consists of noting the length of time required for a steel ball to fall a definite distance through the solution contained in a glass tube of definite uniform diameter, the whole being maintained at a definite constant temperature. Figure 51 shows a typical setup.

The parts used in the standard method have the following specifications:

Length of tube	35.5 cm.
Diameter of tube	2.5 ± 0.05 cm. (0.984 ± 0.02 in.)
Measured distance of fall	25.4 ± 0.08 cm. (10 ± $^1/_{32}$ in.)
Diameter of steel ball	0.793 ± 0.001 cm. (0.3125 ± 0.0005 in.)
Weight of ball	2.0385 ± 0.007 g.

The viscosity determinations are made at a temperature of 25°C. ± 0.1°C. with a stop watch reading to one-fifth of a second. The glass tube contains two etched marks (10 ± $^1/_{32}$ in. apart), each mark being approximately 2 in. from an end of the tube. The viscosity is expressed as the time in seconds for the ball to fall through 10 in. of a solution with the following composition:

Nitrocellulose (dry)	12.2% by weight
Ethyl alcohol	22.0% " "
Ethyl acetate	17.5% " "
Toluene	48.3% " "

TABLE 3

RELATIONSHIP BETWEEN HERCULES NITROCELLULOSE VISCOSITIES AND FIKENTSCHER'S "*k*" VALUES[a]

Hercules viscosity type	"*k*" value × 10^4
30–35 cp.[b]	500–515
$^1/_4$ sec.	605
$^1/_2$ sec.	670
5–6 sec.	865–875
15–20 sec.	950–975
25–30 sec.	995–1010
30–40 sec.	1010–1030
60–80 sec.	1060–1085
125–175 sec.	1120–1150
600–1000 sec.	1245–1285

[a] Values calculated by the authors.

[b] Determined by capillary-tube method.

It has been the practice of one of the principal suppliers of nitrocellulose in Europe to specify viscosities in terms of Fikentscher's[24] "*k*" value. The relationship of the viscosities as determined by the method just described to those in terms of the "*k*" values for different viscosity types of nitrocellulose is shown in Table 3.

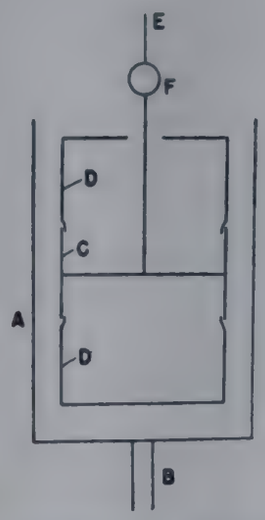
Rotational Viscometers. Viscometers of this type are based on the uniform rotation of solids of revolution about their axes of symmetry. While the most suitable form, from a theoretical standpoint, is that of an ellipsoid of revolution, the constructional difficulties are so great that this shape has not been used widely.

Couette,[48, 49] one of the early workers in the field of viscometry, designed a rotating-cylinder apparatus which is depicted schematically in Figure 52.

[48] M. Couette, *Ann. chim. phys.*, **21**, 433 (1890).

[49] A. Gemant, *J. Applied Phys.*, **13**, 22 (1942).

Another common form is the rotating-disk type of which the MacMichael viscometer is an example. Figure 53 shows the essential parts of this instrument.



A—Cylindrical container.
B—Shaft for rotating A.
C—Inner cylinder concentric with A.
D—Guard rings to minimize end effects.
E—Torsion wire.
F—Mirror.

FIG. 52.—SCHEMATIC DRAWING OF THE COUETTE VISCOMETER (GEMANT[49]).

Still another type of rotational viscometer is based on the rotation of one of two concentric cylinders. Theoretically, it makes no difference if the inner cylinder rotates and the outer is fixed, or vice versa. The

Courtesy of Fisher Scientific Co.

FIG. 53.—THE MACMICHAEL VISCOMETER.[50]

simplest arrangement is that of applying a known torque to the inner cylinder by means of a pulley and weights, and thereafter observing the rate of rotation of this inner cylinder. If the viscosity of the liquid is so

[50] *The MacMichael Viscosimeter*, Bull. No. 560, Eimer and Amend, New York, N. Y.

low that a very low torque must be used to keep the speed of rotation below the value at which turbulence is encountered, the method is unsatisfactory because the friction of the pulleys becomes an important factor. The Stormer viscometer, shown in Figure 54, is an instrument of this type.

Courtesy of Hercules Powder Company

FIG. 54.—THE STORMER VISCOMETER.

This instrument can be used to give readings in absolute units by calibration with liquids of known viscosity. The relationship between the time for a certain number of revolutions and the viscosity can be expressed by the equation

$$\eta = AT - B \tag{26}$$

where A and B are constants whose values depend on the loads used.

The instrument is quite suitable as a general-type viscometer where the highest degree of accuracy is not required. There are a number of moving parts in the apparatus, and it is therefore necessary to guard carefully against frictional losses. It is not suitable for measuring viscosities below 100 centipoises.

Capillary-Tube Viscometers. In the past, it is probable that the greatest number of viscosity measurements, both of solutions and of colloidal suspensions, has been made in capillary-type viscometers in which the viscosity of the liquid under examination has been determined from the dimensions of the instrument. A large number of different types of capil-

FIG. 55.—DIAGRAM OF THE OSTWALD VISCOMETER (BARR[51]).

FIG. 56.—DIAGRAM OF SUSPENDED LEVEL VISCOMETER OF UBBELOHDE (GEMANT[49]).

lary instruments have been designed,[51] in most of which the viscosity determination, while very accurate, involves a high degree of technique and considerable labor. For many technical applications, such viscometers are not practical. As in the case of thermometers, reliance may be placed on standards set up by others. This minimizes the probability of errors due to peculiarities of instrument design, and, in addition, allows viscometers which are suitable for routine measurements to be used.

Probably the best known capillary-tube instrument for practical purposes is the Ostwald viscometer shown in Figure 55. This instrument is merely a pipet viscometer in which there is a submerged discharge into a wide U-tube which is an extension of the capillary. The necessary repro-

[51] G. Barr, *Monograph on Viscometry*. Oxford University Press, London, 1931.

ducibility of level in the wide tube may be obtained by putting a constant quantity of material into it with a pipet.

For this instrument, the following formula applies:

$$\frac{\eta}{\eta_1} = \frac{DT}{D_1T_1} \tag{27}$$

where η and η_1 are the viscosities, and D and D_1 are the densities of two liquids giving times of flow, T and T_1, when equal volumes of the liquids are introduced in the viscometers. If the viscosity of the calibrating liquid is known, it is possible to calculate a constant for the instrument:

$$C = \frac{\eta_1}{D_1T_1}$$

Therefore,

$$\eta = CDT \tag{28}$$

In order to obtain the viscosity of any other liquid or system in this instrument, all that must be known are the time of flow of the liquid through the viscometer and the density of the liquid. It will be noted that there is no kinetic energy correction factor in these equations. This, of course, will be very appreciable at high rates of flow, but may be neglected at moderate or slow rates of flow.

The Ubbelohde viscometer,[51a] shown in Figure 56, is a capillary instrument similar to the Ostwald, but considerably improved in order to permit easier operation, and to eliminate surface tension effects. These improvements are accomplished by venting the capillary at the lower end, and forming the sides of the instrument so that the efflux from the capillary flows away on a hemispherical surface. It has been proved both experimentally and theoretically that surface tension effects can be reduced to a negligible amount, or eliminated by this type of construction. Operation is also simplified, because the size of the sample may be varied within easily observed limits. A kinetic energy correction is, in general, applied to the readings.

For any one instrument, the equation for absolute viscosity may be simplified as follows:

$$\eta = KDT - \frac{CD}{T} \tag{29}$$

where T is the time of flow, D is the density of the liquid, and K and C are constants of the instrument which may be obtained by calibration with a liquid whose absolute viscosity is known. Such liquids may be obtained from the National Bureau of Standards.

[51a] L. Ubbelohde, *Ind. Eng. Chem., Anal. Ed.*, 9, 85 (1937).

Short-Tube or Efflux-Type Viscometers. The short-tube or efflux-type viscometers have been used principally in the petroleum industry. They are exemplified by the Redwood in England, the Engler in Germany, and the Saybolt in this country (Fig. 57). These instruments are called "commercial absolute viscometers"[51] because their standardization depends on dimensions quite carefully specified in the respective countries. The operation and design of the three instruments are similar, but there is a wide difference in detail among them; for example, diameter and length of outlet tube, shape of cup, volume of liquid discharged, etc.

The general type of equation relating absolute viscosities to the time of outflow is of the same type as equation (29).

One of the sources of error in these viscometers is due to the fact that the end of the efflux tube is exposed to the air. This is a serious error where systems containing volatile solvents are used. Another is due to end effects and possible turbulence, both of which are aggravated in short, wide tubes. Additional factors which may have an effect on the measured viscosity are changing hydrostatic head, drainage errors, and the high kinetic energy loss. Cleaning of these tubes also presents some difficulties.

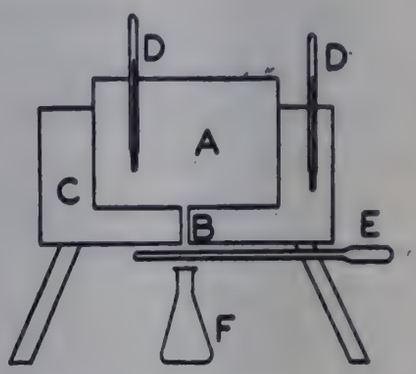


FIG. 57.—DIAGRAM OF TECHNICAL VISCOMETERS OF THE SHORT-CAPILLARY DISCHARGE TYPE (GEMANT[49]).

A—Container for viscous liquid.
B—Capillary tube.
C—Temperature bath.
D—Thermometer.
E—Stop.
F—Flask for collecting efflux from capillary.

Various cups, such as the Parlin, A.S.T.M., and Ford cups, are also short-tube viscometers of the discharge type. They are, however, much cruder than the instruments just described. In these viscometers, the samples are run into cups to the desired level, and the time for the discharge of a specified amount is measured. The readings obtained may be translated into absolute units by means of equations of the type of equation (29).

These viscometers suffer from all the defects of the previously mentioned efflux viscometers, except they are easier to clean. They have, however, one very serious source of error in that, as they are ordinarily used, no means are provided for temperature control. Accurate temperature control in all viscosity determinations is imperative when any degree of accuracy is desired.

Miscellaneous Viscometers. There are several additional instruments which have been described in references[49, 51] previously cited.

(c) *Preparation of Cellulose Solutions*

Solutions of cellulose and its derivatives can be measured in any of the foregoing types of viscometers. Both capillary and falling-sphere instruments have been used more frequently than the rotating-disk or -cylinder viscometers, due chiefly to the fact that greater experimental difficulties are encountered in the operation of the latter types.

The only further item necessary for actual measurement is a suitable solvent for the cellulosic material. Only a relatively small number of solvents for cellulose exist, and, of these, but two types have been found suitable for viscosity measurements. Cellulose is insoluble in both water and ordinary organic solvents. However, certain aqueous salt solutions, such as those of several metallic halides and thiocyanates, and certain aqueous acids, under proper conditions of temperature and concentration, will peptize cellulose. Since, in most of these cases, cellulose decomposes or degrades upon being put into solution, very little use has been made of such solutions for viscosity measurements. Schweitzer's reagent, an aqueous solution of cuprammonium hydroxide, has been used most successfully as a solvent for cellulose in viscosity measurements. Joyner[52] has described a commonly accepted technique for its preparation. Modifications of this method have been given by Small[53] and by the A. C. S. Committee on Viscosity of Cellulose.[47]

The suitability of solvents other than cuprammonium hydroxide for cellulose has been investigated recently. Certain quaternary organic bases, notably dibenzyldimethylammonium hydroxide (manufactured by Röhm and Haas under the trade name "Triton F") have been used successfully. Brownsett and Clibbens,[54] and Russell and Woodberry[55] have compared results obtained with this method with those obtained by the cuprammonium hydroxide method. Solutions of cellulose in Triton F were found to have nearly twice the specific viscosities of corresponding cuprammonium solutions. Straus and Levy[56] have measured the viscosities of solutions of cellulose in aqueous ethylenediamine saturated with cupric hydroxide. Previous workers[54] had had little success with this method because of the apparently inferior solubility of cellulose in this reagent. However, Straus and Levy found that the solvent power of cupri-ethylenediamine solutions is very sensitive to the molar ratio of amine to copper.

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[52] R. A. Joyner, *J. Chem. Soc.*, **121**, 1511 (1922).
[53] J. O. Small, *Ind. Eng. Chem.*, **17**, 515 (1925).
[54] T. Brownsett and D. A. Clibbens, *J. Textile Inst.*, **32**, T57 (1941).
[55] W. W. Russell and N. T. Woodberry, *Ind. Eng. Chem., Anal. Ed.*, **12**, 151 (1940).
[56] F. L. Straus and R. M. Levy, *Paper Trade J.*, **114**, 31 (Jan. 15, 1942).

Cellulose was found to be readily soluble in those solutions in which the molar ratio of amine to copper was exactly 2. This condition is realized when the ethylenediamine solution is completely saturated with cupric hydroxide. Higher specific viscosities were obtained, the determination was considerably more simple and rapid, and was capable of greater reproducibility than in the case of cuprammonium viscosity determinations. The suitability of other organic amines in the presence of cupric hydroxide as cellulose solvents is now being investigated.

Cellulose derivatives, such as cellulose acetate, nitrocellulose, and ethylcellulose, are readily soluble in many ordinary organic solvents and solvent mixtures. Viscosities of solutions of these derivatives may be measured in general, in any type of viscometer.

3. Commercial Utilization of Viscosity

(*a*) *Use in the Textile Industry*

The change in viscosity of cuprammonium solutions of cotton offers the most reliable index of loss of strength due to bleaching and finishing of cotton textiles. The viscosities of solutions of the derived nitrocellulose are also used as indices because they correlate with loss of strength regardless of the type of chemical modification used. However, if the chemical treatment has caused latent damage to the material which is not revealed as a loss in strength, the cellulose cuprammonium viscosity, unlike the nitrocellulose viscosity, may nevertheless decrease to an apparently disproportionate degree, revealing such latent damage. Furthermore, the measurement of viscosity in cuprammonium hydroxide solution is simple and rapid compared with the nitration of the cotton and subsequent determination of nitrocellulose viscosity. The most satisfactory way of estimating extent of damage is to boil the cotton with dilute alkali before making viscosity measurements. In this case, it does not matter which type of viscosity determination is used as far as the results are concerned.

Viscosity measurements on cellulose are also used to determine the spinning qualities of rayon and like materials made from it, as well as the properties of the finished thread or film.

(*b*) *Use in the Pulp and Paper Industry*

The pulp industry uses viscosity measurements on solutions of a given concentration as a control of its product. In the processing of rags or wood pulp, cuprammonium viscosity is considerably decreased by the cooking, bleaching, washing, and beating processes. This decrease is used

as a criterion for the decrease in folding endurance of the paper manufactured from the pulp.

Staudinger and Reinecke,[57] in a discussion of the role of viscosity measurements in the pulp industry, point out that the present technical methods of measuring viscosity can very easily give an incorrect picture of the relationship between viscosity of the pulp and the physical characteristics of paper, fibers, and films made therefrom. One might expect that large changes in viscosity would result in large changes in such physical characteristics, but in many cases this is not true. For example, major differences in the viscosities of certain pulps have been observed, but the characteristics of the paper, films, etc., made therefrom were practically the same in every case.

The fact that technical methods using solutions of the same concentration show differences in viscosity for different samples does not mean there are differences in degree of polymerization (D.P.), as will be understood from the previous discussion on viscosity-concentration relationships. The increase in viscosity with increase in concentration is much greater for products with high values of D.P. than it is for those with low values.

On the basis of data presented on cellulose of various degrees of polymerization, it appears that the technical methods of measuring viscosity can very easily give false results because high-polymer products, changing only slightly in degree of polymerization, can show marked changes in viscosity.

As far as can be determined to date, the relationship between the degree of polymerization and the physical characteristics of products made from the cellulose is not linear. These physical characteristics change markedly in the range of relatively low viscosities, but, after a certain relatively high viscosity is reached, very little change takes place. For example,[58] films cast from nitrocellulose of viscosity below 39 centipoises show zero flexibility and very low tensile strength, while films from a nitrocellulose of 45 centipoises have good flexibility and tensile strengths of several hundred kilograms per square centimeter, an increase of several hundredfold through a very small viscosity rise. Further rise in viscosity up to hundreds of thousands of centipoises produces only a fewfold increase of tensile strength.

(c) *Use in the Plastics, Lacquer, and Varnish Industries*

The use of nitrocellulose for lacquers, etc., requires a relatively low-viscosity product for the following reasons: (1) Less solvent is required

[57] H. Staudinger and F. Reinecke, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 489 (1938).
[58] W. E. Gloor, *Ind. Eng. Chem.*, **27**, 1162 (1935).

than with higher-viscosity products, hence cost is reduced. (2) In the case of lacquers and varnishes, brushing and spraying requirements necessitate a low-viscosity product, yet each coat, when dry, must have a reasonably thick film of plastic material.

A number of processes have been developed for obtaining low-viscosity nitrocelluloses, the most important of which is that of pressure cooking in autoclaves. The nitrocellulose is dispersed in a large excess of water and heated at temperatures from 100 to 150°C. under pressure. The viscosity reduction obtained is determined by the cooking temperature and length of treatment, as well as by the viscosity of the initial material. A considerable decrease in viscosity can be effected without any marked injury to the film-forming properties of the resulting material, as was discussed in the preceding section. Beyond a certain point, however, a further reduction in viscosity causes enough degradation to affect the mechanical properties of the films. Gloor[58] has studied the properties of low-viscosity nitrocellulose in detail.

Fabel,[59] Michel,[60] Mayor,[61] and Gabillion[62] have written extensive reviews of the various processes for lowering the viscosity of nitrocellulose.

Viscosity measurements on ethylcellulose and cellulose acetate are also used as plant controls as in the case of nitrocellulose.

(*d*) *Use in the Explosives Industry*

Olsen and Aaronson[63] have discussed the importance of viscosity measurements in the manufacture of smokeless powder. They point out variations in ballistics which have been found in various batches of powder which were manufactured by the same recipe, and the chemical analyses of which were the same. Many of these variations were traceable to differences in the viscosities of the original batches of cellulose from which the powder was made. Nitrocellulose made from low-viscosity cellulose yields gels which shrink more than those derived from high-viscosity cellulose. Hence, powder grains made from these different materials vary considerably in dimensions, and, therefore, in ballistic properties. At the present time, very close viscosity control is exercised.

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[59] K. Fabel, *Nitrocellulose*, **11**, 103 (1940).
[60] J. Michel, *Rev. gén. mat. plastiques*, **15**, 282 (1939).
[61] Y. Mayor, *Rev. gén. mat. plastiques*, **12**, 199 (1936).
[62] R. Gabillion, *Rev. gén. mat. plastiques*, **7**, 259 (1931).
[63] F. Olsen and H. A. Aaronson, *Ind. Eng. Chem.*, **21**, 1178 (1929).

G. ELASTICITY AND STRENGTH

1. Molecular Factors Affecting Mechanical Behavior

H. MARK

The main reason why natural and artificial cellulose fibers and films are so widely used in industry is their high mechanical strength. It would, of course, be wrong to consider strength as the only important mechanical quality, but it certainly is the outstanding one. Only after the tensile strength of a material has reached a certain value can it be used successfully as a raw material for industrial purposes, and only then do other properties, such as resistance to shear, elongation to break, elastic recovery, and resilience, begin to attract the attention of the producer.

Therefore, it is important to consider to what extent present knowledge allows definite relationships to be worked out between the strength of a material and the nature and structure of the elementary particles of which it is built up. It must be emphasized at the beginning of such a discussion that it is not yet possible to establish reliable quantitative relationships between structure and tensile strength. The reason for this, however, is not so much a lack of insight into the molecular structure of the different materials under consideration, as it is the complicated character of tensile strength as a well-defined physical property.

If mechanical properties such as the compressibility or the modulus of elasticity of simpler substances are considered, it is possible to predict them with a fair degree of accuracy from the atomic or molecular structure of the material. In order to have these fundamental relationships available for further discussion, it is appropriate to give a very brief review of the present knowledge of the mechanical behavior of systems simpler than cellulose.

(*a*) *Elasticity*

Elastic Properties of Simple Substances.

Energy of Cohesion. A very fundamental quantity for the description of the mechanical properties of a single crystal is its energy of cohesion. This

is the total energy needed to evaporate or sublime the crystal into isolated atoms, ions, or molecules. It is usually measured in calories per gram, or in kilogram-calories per mole, and it has been measured experimentally with a high degree of accuracy for many organic and inorganic substances. The present knowledge of the interaction of elementary particles makes possible the computation of the cohesive energy, starting with the lattice structure of the crystal as determined by x-rays and with the different types of interatomic, interionic, and intermolecular forces as given by quantum mechanics.

This cohesive energy can be computed if the potential energy of the crystal lattice is known as a function of the dimensions. The potential energy, in general, will be represented by one component expressing electrical attractive and repulsive forces, and by another component representing attractive or repulsive exchange forces. Born and Mayer,[1] Landshoff,[2] and Hylleraas[3] have calculated the cohesive energy of many ionic crystals using different expressions for the different contributing terms. As shown in Table 1, it is possible to obtain a rather satisfactory agreement of calculated and experimental values. Wigner and Seitz,[4] Seitz,[5, 6] and others[7, 8, 9] have carried out similar calculations for mono- and di-valent metals, and they also have succeeded in obtaining fair agreement with experiment. Finally, for a molecular-type lattice, Sponer and Bruch-Willstätter[10] have computed the cohesive energy of solid carbon dioxide. These results also are contained in Table 1. As yet, no rigorous calculation of the cohesive energy of an atomic crystal such as diamond or SiC has been carried out.

In summary, it may be said that the present expressions for the potential energy function in simple crystals are good enough to allow a rather close calculation of the cohesive energy.

Elastic Constants. In order to obtain more complete knowledge concerning mechanical properties of a substance, the elastic constants, which are connected with the change of the potential energy under the influence of an

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[1] M. Born and J. E. Mayer, *Z. Physik*, **75**, 1 (1932).
[2] R. Landshoff, *Phys. Rev.*, **52**, 246 (1937).
[3] E. A. Hylleraas, *Z. Physik*, **63**, 771 (1930).
[4] E. Wigner and F. Seitz, *Phys. Rev.*, **43**, 804 (1933); **46**, 509, 1002 (1934).
[5] F. Seitz, *Modern Theory of Solids*. McGraw-Hill, New York, 1941.
[6] F. Seitz, *Phys. Rev.*, **47**, 400 (1935).
[7] J. Barden, *J. Chem. Phys.*, **6**, 367 (1938).
[8] E. Gorin, *Physik. Z. Sowjetunion*, **9**, 328 (1936).
[9] W. H. Zachariasen. *J. Am. Chem. Soc.*, **54**, 3841 (1932).
[10] H. Sponer and M. Bruch-Willstätter, *J. Chem. Phys.*, **5**, 745 (1935).

external force, may be calculated. One of the simplest cases is the action of a uniform compression in all directions. In this case, the behavior of a homogeneous material can be described by one single constant: namely, its compressibility. If the initial volume of the sample is V, and the compression produces a volume change of dV and an energy change of dU, then the compressibility, β, of the material is given by

$$dU = \frac{1}{2\beta}\left(\frac{dV}{V}\right) \tag{1}$$

TABLE 1

COHESIVE ENERGIES OF DIFFERENT TYPES OF CRYSTALS (SEITZ[5])

Substance	Cohesive energy (kg.-cal. per mole)	
	Observed	Calculated
LiH	218.5	218
LiF	240.1	242.2
NaCl	183	183
KBr	157.8	161.7
RbI	144.2	148.4
Li	39	36.1
Na	26	23.5
Be	36–53	75
CO_2	8.24	$\cong 7$

If the cohesive energy U of the material is known as a function of the volume V (or, more fundamentally, as a function of the mutual distances of the atoms), the compressibility can be theoretically computed from equation (1) and tested by experiment. Table 2 contains the results of such comparisons. They show that the calculated compressibilities are in reasonable agreement with the experimental values. If the external forces act only in one direction, for instance as stress, two constants are needed to characterize the behavior of a homogeneous material; namely, the *modulus of elasticity* and the *Poisson ratio*. The deformation is described by an elongation parallel to the direction of the stress and by a contraction perpendicular thereto.

If a fiber, whose length L is very large compared with its cross section, is stretched, the modulus of elasticity E can be expressed as[11]

$$E = \frac{P}{q} \cdot \frac{L}{dL} \tag{2}$$

[11] See, for example, W. G. Burgers and J. M. Burgers, *First Report on Viscosity and Plasticity*. 2nd ed., Nordeman, New York, 1938.

where P = acting force in dynes, q = cross section in cm.^{2}, L = original length of specimen in cm., and dL = increase of length in cm. due to the force.

In order to calculate E for any given system, P has to be known as a function of dL. In the range of very small deformations, Hooke's Law can be assumed to be valid:

$$P = f \cdot dL \tag{3}$$

The constant f is characteristic of the material under test and is called the "spring force constant." Equation (3) does not hold for elongations exceeding 1% and can therefore be applied only if the modulus of elasticity is measured by a method which does not involve high strain. The best

TABLE 2

ELASTIC CONSTANTS OF SINGLE CRYSTALS (SEITZ[5])

Substance	Reciprocal compressibility ($1/\beta$) (10^{11} dynes per cm.^{2})	
	Observed	Calculated
Na	0.85	0.88
Cu	13.9	14.1
NaCl	41.6	43.5

method is presumably to measure the velocity with which longitudinal elastic waves (for instance, sound or ultrasonic waves) are propagated in the material. This is usually done by producing a standing wave of a given frequency in the extended filament and by measuring the wavelength with a sensitive detector. The velocity of propagation is then given by the product of the frequency and the wavelength. This measurement was carried out on fibers first by Meyer and Lotmar.[12] Other methods have been applied by various workers,[13–17] but it seems that the figures of Meyer and Lotmar are best adapted for comparison with the value which would be expected from theoretical considerations.

If it is assumed that straight, parallel, hydrocarbon chains extend through-

[12] K. H. Meyer and W. Lotmar, *Helv. Chim. Acta*, **19**, 68 (1936).
[13] W. P. Dreaper and J. G. Davis, *J. Soc. Chem. Ind.*, **31**, 161 (1912).
[14] T. Barratt, *Trans. Faraday Soc.*, **20**, 274 (1924).
[15] J. Karger and E. Schmid, *Z. tech. Physik*, **6**, 124 (1923).
[16] K. C. Brown, J. C. Mann, and F. T. Peirce, *J. Textile Inst.*, **21**, T186 (1930).
[17] H. Mark, *Physik und Chemie der Cellulose*. J. Springer, Berlin, 1932, p. 30, *et seq.*

out the sample (see Fig. 58), there are two changes taking place if a stress acts at the ends of the chains. First, the angle (α) between two subsequent valences can be increased, and, second, the distance (d) corresponding to each valence can be increased.

The spring force constants for both types of deformation can be estimated from the molecular spectra (infrared and Raman) after the break, and valence frequencies of the corresponding vibrations have been calculated with the aid of the relation holding for a harmonic oscillator:

$$f = 4\pi^2 m\nu^2 \qquad (4)$$

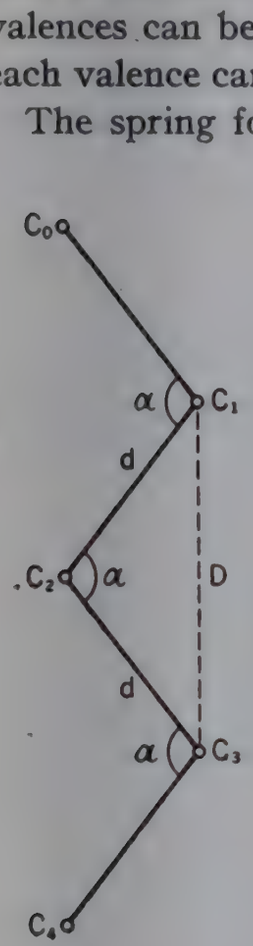

FIG. 58.—DIAGRAMMATIC REPRESENTATION OF A STRAIGHT - CHAIN HYDROCARBON.

C_0, C_1, C_2, C_3, C_4 = Carbon atoms.
d = 1.547 Å.
D = 2.54 Å.
α = 109°30′.

In equation (4), m is the mass of the carbon atom, about 2×10^{-23} g. Valence frequencies are the frequencies with which atoms vibrate along the valence bonds, and break or kink frequencies are those with which the atoms vibrate so that the valence angles change. The latter are found in the range between 9×10^{12} and 2×10^{13} sec.$^{-1}$ while the former lie between 2×10^{13} and 5×10^{13} sec.$^{-1}$. The calculated stress for increasing the valence angles lies, therefore, between 0.5×10^5 and 3.2×10^5 dynes per cm., and that for increasing the valence distances lies between 3.2×10^5 and 20×10^5 dynes per cm.

To calculate the modulus of such systems, P is eliminated from equations (2) and (3), and equation (5) is obtained.

$$E = \frac{L}{q} \cdot f \qquad (5)$$

D in Figure 58 represents the distance between the two carbon atoms 1 and 3 (equal to 2.54×10^{-8} cm.), and q in equation (5) is the cross section of one chain (equal to about 25×10^{-16} cm.^{2}). By substituting these numerical values in equation (5), the modulus of elasticity is obtained:

For increasing the valence angles: 4×10^{11} to 25×10^{11} dynes per cm.^{2}
For increasing valence distances: 2.5×10^{12} to 20×10^{12} dynes per cm.^{2}

If both mechanisms are arranged in series, as they obviously are in an extended linear hydrocarbon chain, the smaller modulus would be expected to be the controlling one, and hence the values should be between

4000 and 25,000 kg. per mm.^{2} or between 6×10^6 and 3.8×10^7 lbs. per sq. in.

Elasticity of Cellulose. Meyer and Lotmar[12] have carried out a very accurate calculation of the elastic modulus of cellulose, using the model represented in Figure 59. The elastic force of the —C—C— bonds was assumed to be 4.3×10^5 dynes per cm. and that of the —C—O— bonds as 5×10^5 dynes per cm. The calculations were made both for the valence force system of Bjerrum,[18] in which the bonds between adjacent atoms are characterized by certain definite angles between each other, and for a system obeying the rule of Bartholomé and Teller,[19] which applies to the intensities of the different lines in the Raman spectra. In each case, the elastic modulus of cellulose was found to be between 7900 and 12,300 kg. per mm.^{2}.

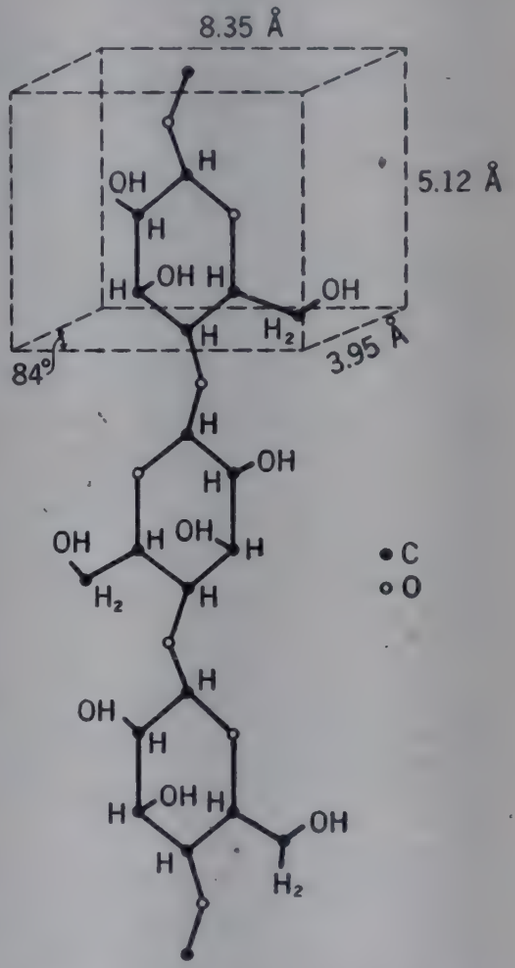

FIG. 59.—MODEL OF THE CELLULOSE CHAIN (MEYER AND LOTMAR[12]).

Table 3 contains a series of experimentally observed moduli of elasticity. It can be seen that these values are in as fair an agreement with the theoretical computations as can be expected. It may be added that this agreement is found not only in the case of cellulose, but also in the case of other carefully investigated high-polymeric substances. This may be considered as another indication that the main valence chain or net theory of these substances represents a reasonable approach to their true structure. If any kind of van der Waals' forces were assumed to be responsible for the modulus of elasticity, values between 3×10^3 and 12×10^3 dynes per cm. would be expected, and not the high moduli actually observed by various authors.

Equation (5) shows that two factors are mainly involved in building up a high modulus; namely, the elastic force of the weakest bond (smallest value of the spring force constant) and the tightness of the packing (the reciprocal of q). If the f-values of two materials such as cellulose and cellu-

[18] N. Bjerrum, *Ber. deut. physik. Ges.*, **16**, 737 (1914).

[19] H. Bartholomé and E. Teller, *Z. physik. Chem.*, **B19**, 366 (1932).

lose butyrate or vinyl alcohol and vinyl acetate, are comparable, the moduli may still vary a great deal because of the differing densities of each arrangement. If a material with a very high modulus (rigid and stiff) is desired, the chains must be drawn parallel to each other and must be packed as tightly as possible.

TABLE 3

MODULI OF ELASTICITY OF REPRESENTATIVE CELLULOSE SPECIMENS

Substance	Modulus of elasticity			Observer
	Dynes per cm.^{2}	Kg. per mm.^{2}	Lbs. per sq. in.	
Ramie, native wet	1.9×10^{11}	1900	27×10^5	Meyer and Lotmar
Ramie, native air-dry	5.2×10^{11}	5200	75×10^5	Meyer and Lotmar
Ramie, native dry	6.0×10^{11}	6000	85×10^5	Meyer and Lotmar
Ramie, native mercerized	8.2×10^{11}	8200	120×10^5	Meyer and Lotmar
Ramie, native at −190°C.	$4–5.5 \times 10^{11}$	4000–5500	$60–80 \times 10^5$	Valko
Cotton, native	5.0×10^{11}	5000	70×10^5	Barrath
Flax, native	$8–11 \times 10^{11}$	8000–11,000	$110–160 \times 10^5$	Meyer and Lotmar
Viscose rayon, highly oriented	2.5×10^{11}	2500	35×10^5	Karger and Schmid
Viscose rayon, highly oriented	3.4×10^{11}	3400	50×10^5	Meyer and Lotmar
Viscose rayon, dry	6×10^{11}	Up to 6000	80×10^5	
Viscose rayon, normal	8×10^{11}	850	12×10^5	Karger and Schmid
Viscose rayon, normal	1.2×10^{11}	1170	17×10^5	Meyer and Lotmar
Viscose rayon, dry	1.6×10^{11}	1600	25×10^5	Meyer and Lotmar

The product with the highest possible density is, of course, the one with the highest possible degree of crystallinity. On the other hand, softer, more extensible products can be obtained by avoiding too high moduli through a lesser degree of orientation and, thus, by looser packing.

De Boer,[20] working from a slightly different point of view, has developed

[20] J. H. de Boer, *Trans. Faraday Soc.*, **32**, 10 (1936).

a very thorough treatment of the elastic properties of high polymers. He assumed a similar elastic force for the —C—C— bond, took for q the value 14×10^{-16} cm.^{2}, and obtained for a phenol-formaldehyde resin a modulus of 11,000 kg. per mm.^{2}. This value agrees satisfactorily with the others calculated and with the experimental ones of Table 3. It does not, however, agree with the moduli which have actually been measured on phenol- and cresol-formaldehyde polymers by Houwink.[21, 22] The highest values ever observed are between 800 and 1000 kg. per mm.^{2}, and hence they are only one tenth of the calculated ones. This is presumably due to the fact that, in the actual sample, the chains never exhibit a packing which is as ideal as the one on which the calculations are based. There will always necessarily be certain displacements and distortions in the geometrical fitting of adjacent molecules which will be more pronounced in a random three-dimensional network than in a highly oriented and crystallized straight-chain polymer. The number of covalent bonds passing through the unit cross section is, therefore, presumably much smaller than 7×10^{14} as assumed above. The remainder of the chains are held together by van der Waals' forces, which have an elastic modulus around only 100 kg. per mm.^{2}, and hence the average value of the modulus of elasticity is very distinctly reduced.

In summary, it may be said that, through certain simplifying assumptions, the elastic constants of ionic, metallic, and long-chain substances can be calculated and that samples exist whose properties agree fairly well with the calculated values.

However, it must be emphasized that the elastic modulus of fibers shows little direct connection with properties such as tenacity, elongation to break, and elastic recovery, which are of most importance technically. There still remains the real goal of deducing these properties as a consequence of molecular structure and of calculating the values quantitatively. In order to see how far this can be achieved, it is appropriate to start again with the discussion of single crystals such as NaCl, diamond, and metals.

(*b*) *Tensile Strength*

Tensile Strength of Single Crystals. The potential energy between two halves of a rocksalt crystal separated by a (100) plane is given, according

[21] R. Houwink, *Trans. Faraday Soc.*, **32**, 122, 131 (1936).

[22] R. Houwink, *Elasticity, Plasticity and Structure of Matter*. University Press, Cambridge, 1937.

to de Boer,[20] by a curve of the type shown in Figure 60A. There is a minimum when the interatomic distance (r) is about 2.8×10^{-8} cm. (equilibrium position), a very steep slope on the compression side (low values of r), and a more gradual rise of the potential as r increases (as the crystal is stretched). By differentiating the potential energy curve of Figure 60A, one gets the force f as a function of r (Fig. 60B). This force is zero for the

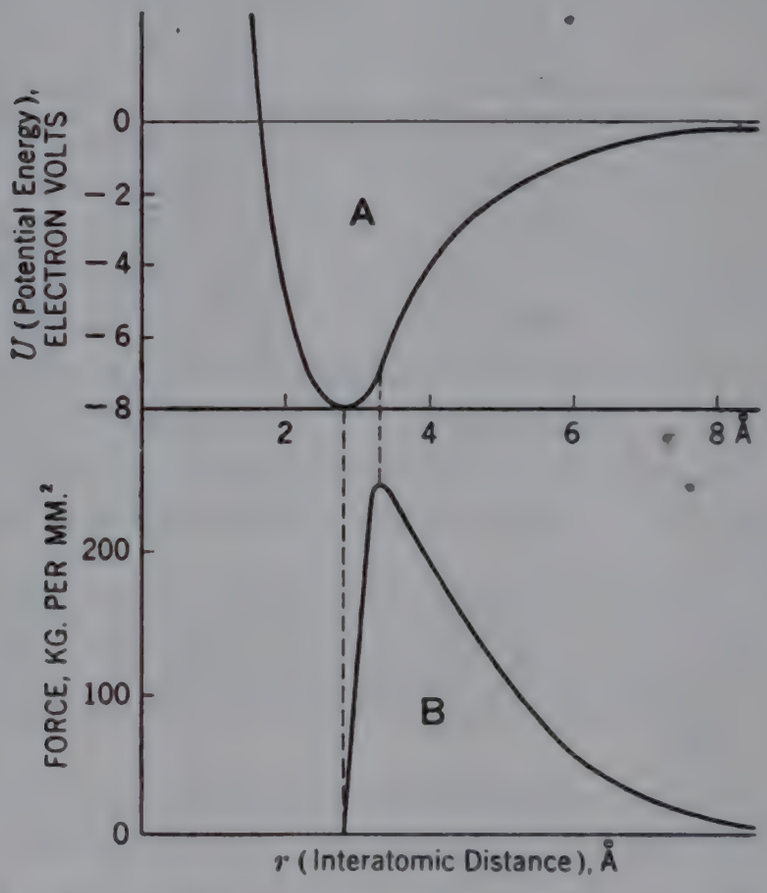

FIG. 60.—POTENTIAL ENERGY AND FORCE BETWEEN TWO HALVES OF A NaCl CRYSTAL, SEPARATED BY A (100) PLANE (COMPARE DE BOER[20]).

equilibrium position $r = 2.8$ Å. and again for $r \cong 6$ Å., and it has a maximum around $r = 3.3$ Å. The value of this maximum is the force necessary to separate the two halves of the crystal; that is, it is the theoretical tensile strength. It amounts, as is shown in Figure 60B, to about 2.4×10^{10} dynes per cm.^{2}, or 240 kg. per mm.^{2} (3.5×10^5 lbs. per sq. in.). The experimental values are around 5×10^7 dynes per cm.^{2} (0.5 kg. per mm.^{2}, 700 lbs. per sq. in.). This is about 500 times smaller than the theoretical, a discrepancy which has aroused very much attention and has been dis-

cussed particularly by Griffith,[23] Joffé,[24] Polanyi,[25] Smekal,[26] and Zwicky.[27] The proposed, and generally accepted, explanation is that all real crystals have either small incidental surface cracks or more or less regularly distributed flaws and defects of the crystal structure, so that the rupture starts at a weak spot and continues from there through the whole sample. Every theoretical value for the tenacity can therefore be considered only as an upper limit, and the ratio between the theoretical and actual (technical) tensile strength becomes a measure of the presence of imperfections and irregularities in the structure of the samples under investigation.

This fact shows that a theoretical calculation of the tenacity of high polymers can give a result of only limited significance. Nevertheless, it has been attempted by Mark,[28, 29] Meyer,[30] and de Boer,[20] and has yielded certain points of interest.

Tensile Strength of Cellulose and Its Derivatives. In order to start a calculation of the tensile strength of cellulose and its derivatives, certain assumptions have to be made. Two cases, which seem to be of interest, will be discussed. The first assumes that rupture is due only to a break of the chains themselves, while the second assumes that it is due solely to slipping of the chains along each other.

Rupture of Primary Valences. A first approximation to the order of magnitude of the tensile strength in this case may be obtained in the following simple way: Assume that a fiber consisting of infinitely long cellulose chains is subjected to a stress at its ends parallel to the direction of the chains. If all chains are parallel and arranged according to the structure of the lattice of native cellulose, their individual cross section is 33×10^{-16} cm.^{2}, and hence the number n of chains passing perpendicularly through the unit cross section of 1 cm.^{2} is 3×10^{14}. If the chains are not completely oriented, or if they are oriented but not crystallized, n will assume smaller values.

The force necessary to break one cellulose chain must next be calculated.

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[23] A. A. Griffith, *Phil. Trans. Roy. Soc.*, **221**, 163 (1920).

[24] A. F. Joffé, *The Physics of Crystals*. McGraw-Hill, New York, 1928.

[25] M. Polanyi, *Naturwissenschaften*, **9**, 288 (1921).

[26] A. Smekal, *Physik. Z.*, **34**, 633 (1933).

[27] F. Zwicky, *Physik. Z.*, **24**, 131 (1923); *Helv. Phys. Acta*, **3**, 269 (1930).

[28] H. Mark, *Melliand Textilber.*, **10**, 695 (1929); *Paper Trade J.*, **113**, 34 (July 17, 1941).

[29] H. Mark, *High Polymers*, Vol. 2, *Physical Chemistry of High Polymeric Systems*. Interscience, New York, 1940.

[30] K. H. Meyer, *High Polymers*, Vol. 4, *Natural and Synthetic High Polymers*. Interscience, New York, 1942.

The most labile points in the chain will obviously be the —C—O—C— bridges which connect the glucose rings. The energy of the —C—O— bond is about 90 kg.-cal. per mole or 6×10^{-12} ergs per individual bond, and it is equal, approximately, to the product of the force necessary to separate the atoms and the distance from the equilibrium position to the point where the interatomic attractive force is essentially zero. Substituting numerical values, equation (6) is obtained:

$$6 \times 10^{-12} \text{ ergs} = \text{force} \times (4.0 - 1.5) \times 10^{-8} \text{ cm.} \qquad (6)$$

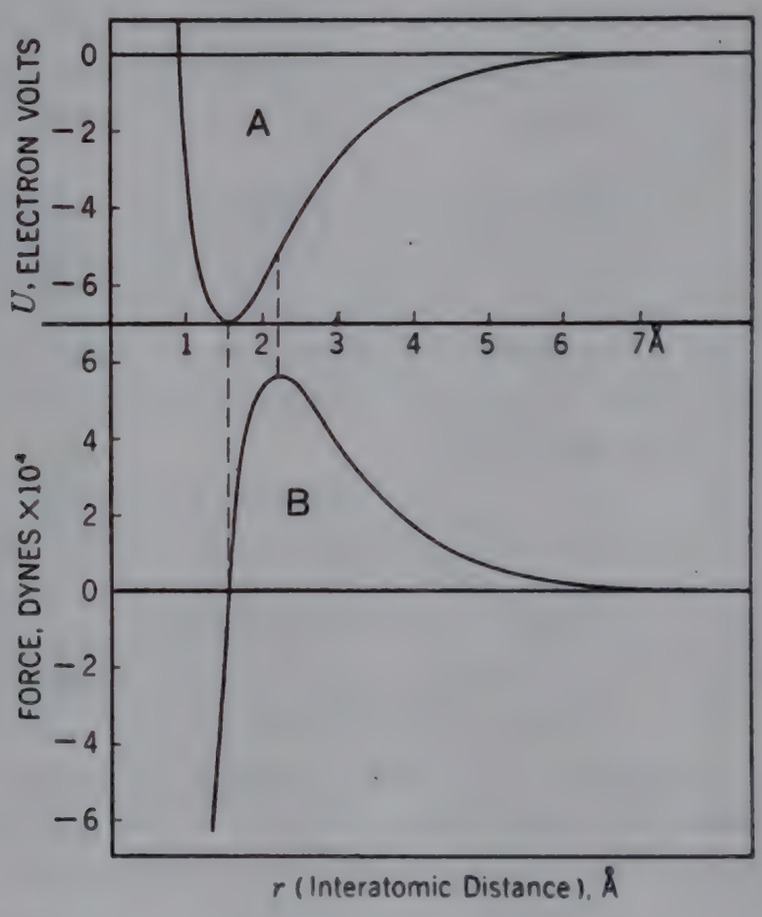

FIG. 61.—POTENTIAL ENERGY AND FORCE BETWEEN TWO ALIPHATIC BOUND CARBON ATOMS (DE BOER[20]).

1.5 Å. is the equilibrium distance of the —C—O— bond, and 4.0 Å. is the distance at which the bond can be considered broken. From equation (6) the tenacity of one single cellulose chain is, of course, easily calculated; it is 2.4×10^{-4} dynes. The tensile strength t_s of this idealized sample is obtained through multiplication by n.

$$t_s = 2.4 \times 10^{-4} \times 3 \times 10^{14} = 7.2 \times 10^{10} \text{ dynes per cm.}^2 \cong 60 \text{ g. per denier}^*$$

This is about eight times higher than the maximum values measured with

* Denier is the weight in grams of 9000 meters of a single- or multiple-fiber yarn.

well-oriented and highly-crystallized natural and artificial fibers such as flax, hemp, or viscose rayon.

In equation (6), the force is assumed to be constant over the range from $r = 1.5$ Å. to $r = 4.0$ Å. This assumption, of course, is not correct. A better approximation to the tensile strength is obtained by starting with the potential energy curve of the —C—O— bond, deriving from it the force as a function of r, and taking the maximum of this curve. Figure 61 shows, according to de Boer,[20] the potential energy U between two aliphatic carbon atoms in electron volts (Curve A), and the force in dynes (dU/dr) (Curve B), both as a function of the interatomic distance (in Å.). The aliphatic —C—C— bond is here substituted for the β-glucosidic —C—O— bond,

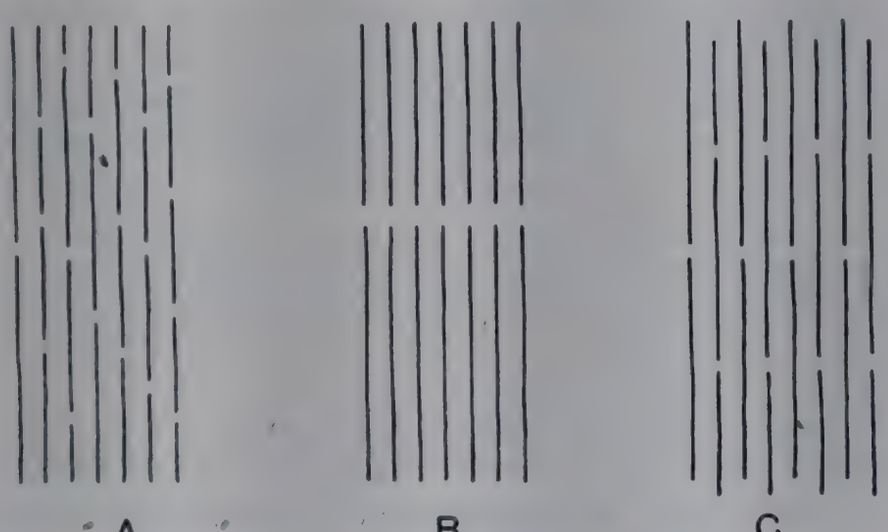

FIG. 62.—SCHEMATIC DIAGRAM OF COMPLETELY PARALLEL CELLULOSE CHAINS.

A—Random overlapping; B—No overlapping; C—Regular overlapping.

because its potential energy function is better known. There is no reason to assume that this substitution should falsify the result appreciably. Curve B of Figure 61 shows that the maximum force is 5.6×10^{-4} dynes, which is about twice the value of the approximate calculation. Hence, this approach leads to still higher values for the tenacity of an idealized cellulose sample (about 1500 kg. per mm.^{2} or 120 g. per denier). This result presumably indicates that all real samples break according to a different mechanism.

Rupture of van der Waals' Forces. Assume now a sample of completely parallel cellulose chains with finite length, overlapping each other irregularly, as shown schematically in Figure 62A. A minimum value for the tenacity of this system will obviously be found if there exists somewhere in the sample a cross section without any overlapping, such as is shown in

Figure 62B. The tenacity of this cross section can be figured out in the same way as above, using $n = 3 \times 10^{14}$ as the number of chains per cm.^{2}, but taking into account van der Waals' forces instead of the forces of covalent bonds.

The values to be substituted in the equations are:

energy per bond = 4000–5000 cal. per mole = 3×10^{-13} ergs per bond
equilibrium distance = 3.5 Å.
distance at which the force seems to act = 7.0 Å.

Hence:

$$\text{force} = \frac{3 \times 10^{-13}}{3.5 \times 10^{-8}} = 0.9 \times 10^{-5} \text{ dynes per bond}$$
$$= 2.7 \times 10^{9} \text{ dynes per cm.}^2$$
$$\cong 2 \text{ g. per denier}$$

Values of similar order of magnitude have been obtained by de Boer[20] using the potential energy curve for the van der Waals' attraction.[31]

It can be seen that these figures (2 g. per denier) are in fair agreement with the tenacity of very dry, poorly oriented viscose or acetate rayon filaments. This may be an indication that in these cases the rupture actually occurs through the breaking of van der Waals' (sometimes perhaps also hydrogen) bonds.

In order to account for the high tenacities (up to 6 or 7 g. per denier) which are obtained if fibers of better orientation are investigated, it seems reasonable to assume that, as the chains and crystallites become more and more parallel, the probability of finding one cross section which contains only chain ends will decrease rapidly. With increasing overlapping of the chains, the ragged cross-sectional area over which only van der Waals' forces need to be broken will increase, and, with it, the number of bonds which have to be broken will be larger also. In other words, if the covalent bonds are so strong that they do not rupture, van der Waals' forces must be opened over a much larger area because the chains are overlapping each other in an irregular way. Instead of breaking 3×10^{14} van der Waals' bonds along a smooth cross section (as shown in Fig. 62B) in one and the same instant, those parts of the chains which overlap must tear loose and slip along each other.

Slippage of Chains. In order for two chains to slip along each other (as shown in Fig. 63), it is obviously not necessary that the full strength of the

[31] Cf. references 32, 33, 34.

[32] J. E. Lennard-Jones, *Proc. Phys. Soc.* (*London*), **43,** 461 (1931).

[33] F. London, *Z. physik. Chem.*, **B11,** 222 (1931).

[34] J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37,** 682 (1931).

van der Waals' forces along the whole distance of 3.5 Å. be overcome and that the attracting groups A_1 and A_1' be removed completely from each other's sphere of action. It is necessary only that the chains become uncoupled. This requires a certain activation energy, sufficient to let A_1 move to A_2, then to A_3, and so on, and to carry out the elementary step of slippage under the influence of the stress. This concept is similar to the very promising way in which Eyring and his collaborators[35] have treated the viscosity of liquids as a rate phenomenon ("theory of holes"). It has been shown recently by Kistler[36] that the flow of high polymers can also be described very successfully with the aid of these ideas. If activation energies are assumed to be of the same order of magnitude as those which are responsible for the viscosity of substances containing OH groups (water or glycerol, for instance), the force to produce the first step in slipping is of the order of magnitude of 10^{-7} dynes, which agrees with an estimation made by Meyer[30] and Mark[29] several years ago.

FIG. 63.—SCHEMATIC DIAGRAM OF THE SLIPPAGE OF TWO CELLULOSE CHAINS, SHOWING THE CENTERS OF ATTRACTION.

If, as an example, an idealized system of regularly overlapping chains having a degree of polymerization of 400 (Fig. 62C) is considered, all van der Waals' bonds between the ends of the chains must first be ruptured. According to the previous calculation, this leads to a tenacity of about 27 kg. per mm.^{2} (2 g. per denier). Then the remaining chains must be torn loose from each other along the distance of their mutual overlapping. This distance will correspond to 200 glucose residues for each chain in the idealized case. If every glucose residue is assumed to have four centers of attraction (three OH groups and one —C—O—C— group), 800 centers of attraction in each chain must be uncoupled. Having 3×10^{14} chains per cm.^{2}, the force necessary to produce slipping can be estimated as follows:

$$S \text{ (slipping)} = 800 \times 3 \times 10^{14} \times 1/2 \times 10^{-7} = 9 \times 10^9 \text{ dynes per cm.}^2$$
$$\leqq 8 \text{ g. per denier}$$

When to this slippage value is added the force which is necessary to break all chain-end bonds, the final tenacity values are around 10 g. per

[35] H. Eyring, R. E. Powell, and W. E. Roseveare, *Ind. Eng. Chem.*, **33**, 430 (1941).
[36] S. S. Kistler, *J. Applied Physics*, **11**, 769 (1940).

denier. They are about 50 to 100% higher than the tenacities of highly oriented and crystallized viscose rayon fibers, but only 30% higher than the strength of the best natural samples such as flax or hemp.

It is the belief of the writer that the accuracy of the above calculations is determined by the extent to which the model of Figure 62C represents the relationship of the tensile strength of a cellulose filament to its molecular structure. It seems to be not unreasonable that artificial fibers never reach the theoretical values because, considering all the chemical and physical changes of the filament during spinning, it would seem very improbable that an arrangement as ideal as the one represented in Figure 62C can ever be attained along the entire length of a macroscopic sample.

The limit of the technical strength of fibers appears, therefore, always to be the extent of the imperfections in crystallizing the chains and orienting the crystallites, just as the limit of the technical strength of ionic crystals and metals is the extent of the irregularities in the structure of these substances. It is obvious that the strength of textile fibers will be determined by those parts which deviate most from the ideal conditions as depicted in Figure 62C. If a thin slice is taken from a filament, certain parts of this cross section are well crystallized, oriented, and overlapped and therefore will stand the stress which is applied to them. Other parts, however, which are of less favorable structure (no orientation and no overlapping) will give way and unload themselves at the expense of the stronger portions. As a consequence, the stress in these portions will increase unduly and produce the break earlier than if the whole cross section were homogeneous. Thus, the rupture of a high-polymeric system has to be treated by assuming that it starts at the weakest link and progresses gradually to the stronger portions, the strength of which may be completely prevented from adding to the numerical value of the tenacity.

Considerations of this type will be discussed more thoroughly in Section G, 2 of this chapter, which deals with the mechanical properties of filaments and films. In this section on the molecular factors affecting mechanical behavior, the influence of different structural features on tensile strength will now be discussed.

Influence of Structural Factors on Tensile Strength. The main factors which will be discussed under this heading are: chemical characteristics of the chains, average chain length, distribution curve of chain length, orientation, and crystallization.

Chemical Characteristics of the Chains. The magnitude of the forces between the chains, the flexibility of the chains, and the way in which the attraction centers are distributed along the chains seem to be of particular

importance. At first sight it would seem that the magnitude of the mutual attraction would be by far the most important factor. This, however, may not be true when the chains become particularly bulky and inflexible. In such cases, even strong forces may be counteracted by the great difficulties of fitting the individual molecules into a regular pattern.

The forces which represent one extreme are those between polyhydrocarbon molecules, where the mutual attraction of groups such as —CH_3, —CH_2—, or =CH— is very small (about 1000 cal. per mole of these groups). Such materials have low moduli of elasticity in the uncrystallized and unoriented state (10^6 to 10^7 dynes per cm.^{2}) while in the fully crystallized state the moduli may be 10^{11} to 10^{12} dynes per cm.^{2} The extent to which flexibility of the chains affects the properties of polyhydrocarbons may be seen from the distinct difference in the behavior of rubber, gutta-percha, and polystyrene. The influence of more or less complete geometrical packing becomes apparent if polyethylene or gutta-percha is compared with copolymers of butadiene and styrene or other vinyl derivatives. The straight, homogeneous chains of the two former substances can be packed more easily into a lattice than can the comparatively irregular copolymers, and, hence, the former exhibit the properties of a plastic more than those of a rubber. In all these cases of comparatively weak intermolecular attraction, the entropy terms apparently play an important role.

If, on the other hand, the intermolecular forces are strong, as in cellulose, proteins, polyamides, or polyvinyl alcohol, they determine the behavior of the material to a large extent. Even here, the flexibility of the chains affects the properties remarkably, as may be seen by comparing cellulose with polyvinyl alcohol. In the bone-dry state, both substances show typical fiber properties, having high strength and comparatively low elongations. If wetted out, cellulose, with its inflexible chains, does not change properties considerably, while polyvinyl alcohol, having very flexible individual chains, assumes distinctly rubber-like properties. It is not possible as yet to calculate the free energy of a polymeric material as the sum of appropriate potential energy and entropy terms, and, at present, a preliminary and rather uncertain method must be used to estimate the counteracting influence of the different factors.

The extent of the action of the forces between chains can be roughly estimated by using the molar cohesion between the active groups which are distributed along the chains. This molar cohesion is given in calories per mole of such groups and has been derived by Dunkel[37] and Meyer[30]

[37] M. Dunkel, *Z. physik. Chem.*, **A138**, 42 (1928).

from thermodynamic considerations of the vapor pressure and boiling points of a group of representative substances. Table 4, containing some of the numerical data, shows that the different groups have very different values.

While there is a certain amount of quantitative information on the magnitude of the forces, there is practically none concerning the influence of the entropy terms. All that can be done is to classify the materials into those which have more flexible and those which have less flexible chains, in which case cellulose presumably is one of the most rigid chain molecules. The different polymers can further be classified into those in which

TABLE 4

MOLAR COHESION OF DIFFERENT GROUPS

Group	Molar cohesion, kg.-cal. per mole	Group	Molar cohesion, kg.-cal. per mole
$-CH_3$ } $=CH_2$ }	1800	$-COOCH_3$	5600
		$-COOC_2H_5$	6230
$-CH_2-$ } $=CH-$ }	1000	$-NH_2$	3530
		$-Cl$	3400
$-O-$	1630	$-F$	2100
$-OH$	7250	$-Br$	4300
$=CO$	4270	$-I$	5000
$-CHO$	4700	$-NO_2$	7200
$-COOH$	8970	$-CONH-$	10,600

the attractive centers are regularly distributed along the chain, so that they easily meet the geometrical requirements for a close packing, and into those where this is not the case. Cellulose seems to be an easily crystallizable substance, and cellulose triesters also seem to belong to this group. On the other hand, partly esterified or etherified cellulose apparently packs less readily. In general, rigid chains have higher melting points and less solubility than flexible ones, even if the forces are equal, because the entropy gain upon melting, swelling, or dissolving, is smaller. It would be expected, of course, that a material with better packing would be higher melting and less soluble than another one with less favorable structure, even if the interchain forces were equal.

Finally, it must again be emphasized that there is practically no quantitative material available to give indications of the influence of the chemical nature of the different parts of a long-chain molecule (which nature is determined by the type of attractive groups, by the distribution of the

groups, and by the internal flexibility of the chain) on the mechanical and thermal behavior of a given system.

Average Chain Length. Much interesting and important experimental data have been collected on the question of how the average chain length of a given material influences the mechanical properties.[28, 38–46] In most cases, a technical raw material was fractionated either by selective solubility or by gradual precipitation. The different fractions were separated, spun into filaments, or cast in films, and were mechanically tested. Such experiments were carried out with cellulose and its derivatives, polyvinyl acetate, and polyesters. Nevertheless, it must be pointed out that all these investigations can only be considered as a first step in discovering the general law which governs the relationship between average chain length and tenacity, because in no case were all necessary precautions taken nor were all details cleared up. First of all, the quantity of the fractionated material available for mechanical testing was always small, and hence the data which have been collected concerning tenacity, elongation, and other properties have been insufficient. The determination of the chain lengths of the different fractions was usually only a rough one, and the homogeneity of the fractions was not investigated by separate experiments. The different fractions were usually spun or cast under identical conditions, although they might have developed their most favorable mechanical properties under different spinning and casting conditions. The small quantity of material available did not allow a more systematic study.

These critical remarks, of course, are not intended at all to minimize the interest and importance of the investigations referred to; they merely stress the points on which improved and advanced study would be most welcome.

Based on the results available at present, the situation is as follows. First, there is a certain minimum value of degree of polymerization (D.P.) necessary for the sample to develop mechanical strength at all.

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[38] W. H. Carothers and F. J. Van Natta, *J. Am. Chem. Soc.*, **55**, 4714 (1933).

[39] S. D. Douglas and W. N. Stoops, *Ind. Eng. Chem.*, **28**, 1152 (1936).

[40] H. Lachs, J. Kronman, and J. Wajs, *Kolloid-Z.*, **79**, 91 (1937); **84**, 199 (1938); **87**, 195 (1939).

[41] F. Ohl, *Kunstseide*, **12**, 468 (1930).

[42] E. Ott, *Ind. Eng. Chem.*, **32**, 1641 (1940).

[43] H. J. Rocha, *Kolloidchem. Beihefte*, **30**, 230 (1930).

[44] H. M. Spurlin, *Ind. Eng. Chem.*, **30**, 538 (1938).

[45] H. Staudinger, *Die hochmolekularen organischen Verbindungen.* J. Springer, Berlin, 1932.

[46] E. Steinberger, *Physics*, **5**, 53 (1934).

This critical D.P. varies with the chemical nature of the material; it is presumably lowest with polyamides and cellulose, and highest with hydrocarbons. It extends from D.P. of about 35 in the former cases to about 85 in the latter. No attempt has yet been made to relate this critical value quantitatively to the chemical character of the chains as discussed earlier in this section, but it seems to be safe to consider its existence as an empirical fact.

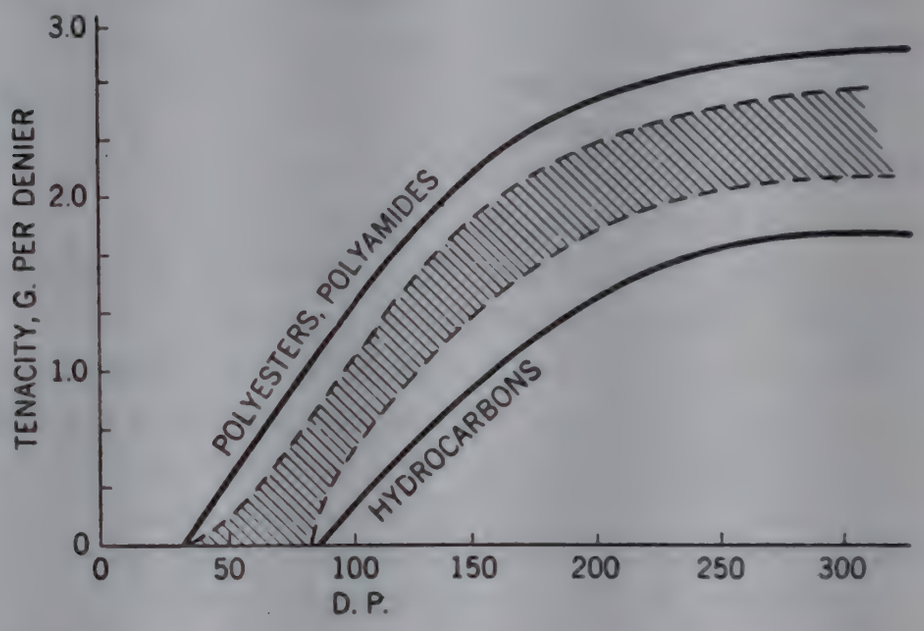

FIG. 64.—RELATIONSHIP OF TENACITY TO DEGREE OF POLYMERIZATION FOR HIGH-MOLECULAR-WEIGHT COMPOUNDS.

Second, beyond this critical value and up to a D.P. of 200, the mechanical properties, such as tenacity (tensile strength) and folding strength, increase roughly proportionally to increasing chain length. It seems that the slope of this increase again depends upon the chemical nature of the material under consideration; chains with strong intermolecular forces having a steep slope, chains with weak ones, a flatter slope.

Last, after a D.P. of around 200 is reached, the curve of tenacity versus chain length flattens out, and a limit of saturation is reached, above which the average chain length does not influence the mechanical properties to a further considerable degree. Again it seems that this limit depends upon the chemical nature of the investigated material. The saturation is established at high values of tenacity for chains having strong attractive centers, while it is established at higher D.P.'s and at lower tenacities for substances such as cellulose butyrate or hydrocarbons.

The relationship of tenacity to D.P. is diagrammed in Figure 64. It must be emphasized that this figure does not represent experimentally measured

curves entirely. It gives more a picture of extrapolated knowledge rather than established facts. Part of the area between the two extreme curves has been shaded. This part represents the one in which there is at least a certain number of experimental points, while, on both sides of it, there are only a very few indications as to the behavior of the materials. Considering the fundamental character of such a diagram, it certainly would be very desirable to be able to draw it with better accuracy and reliability.

Distribution Curve of Chain Length. Unfortunately, only a little reliable information exists as to the influence of the chain-length distribution on the mechanical properties. In some cases, the tenacity, elongation, and folding strength of fractions have been compared with the corresponding values of the unfractionated material, but no real systematic attempt has been made to build up distribution curves of distinctly different shape, and to compare the mechanical properties of samples which have been spun or cast of such materials.[47]

However, Spurlin,[44] Schieber,[49] and others[28] have recently carried out experiments which give at least a limited insight into the effect of chain-length distribution on the mechanical behavior. All that may be concluded with certainty from these studies is that tenacity, elongation, and folding strength are distinctly decreased if the sample contains 10 to 15% of chains below a D.P. of around 100. Such low-molecular-weight fractions seem to affect all mechanical properties adversely, although nothing can yet be said about the quantitative relationship between the amount of this low fraction and the tenacity of the material.

Orientation. Herzog[50] and Lilienfeld[51] were the first to observe that orientation of the crystallized part of a cellulose sample has much influence on its mechanical properties. Improved alignment of the crystallites parallel to the fiber axis increases the tenacity very distinctly, while it decreases the elongation and the resistance to shear. Oriented films show a marked anisotropy, having large values for the tenacity parallel to the direction of the orientation, and low values perpendicular thereto. Tables 5A and

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[47] In this connection, R S. Neiman[48] has recently published the results of a more comprehensive study of tensile strength and chain length distribution. These papers could not be included in this article because only the abstracts were accessible at the date of writing. It seems that the results of these recent investigations agree with the point of view adopted in this chapter.

[48] R. S. Neiman, Z. Rogowin, and R. Obogi, *Org. Chem. Ind.* (U. S. S. R.), **2**, 461 (1936); R. S. Neiman and E. A. Fokina, *Org. Chem. Ind.* (U. S. S. R.), **5**, 742 (1938).

[49] W. Schieber, *Zellwolle*, **5**, 266 (1939).

[50] R. O. Herzog, *J. Phys. Chem.*, **30**, 457 (1926).

[51] L. Lilienfeld, Brit. Patents 274,521 (Jan. 11, 1926); 274,690 (Jan. 11, 1926).

5B and Figures 65A and 65B show a few data which serve to illustrate this effect quantitatively. Very highly stretched viscose and acetate rayon filaments reach tenacities up to 7 g. per denier, while the elongation to break goes down to 2 or 3%. Native cotton also is stronger if better oriented. Berkley[52] and Kerr[53] have recently shown very convincingly that this relationship exists, and they have even used the orientation of a sample to predict its tenacity successfully.

TABLE 5A

INFLUENCE OF ORIENTATION ON TENACITY

Substance	Tenacity, g. per denier
Viscose rayon, poorly oriented	1.7–1.9
Viscose rayon, moderately oriented	2.0–2.6
Viscose rayon, highly oriented	3.0–3.5
Viscose rayon, extremely oriented	up to 5.8
Acetate rayon, poorly oriented	1.3–1.6
Acetate rayon, moderately oriented	1.8–2.3
Acetate rayon, highly oriented	3.5–4.0

TABLE 5B

INFLUENCE OF STRETCHING OF A FILM ON ITS TENACITY IN DIFFERENT DIRECTIONS

Angle between the direction of stretching and a given direction in the sheet	Tenacity before stretching, kg. per mm.^{2}	Tenacity after stretching, kg. per mm.^{2}
0°	11.6	26.5
30°	11.2	15.7
60°	11.4	10.2
90°	11.5	4.5
120°	11.9	9.3
150°	11.2	14.7
180°	11.1	25.9

Qualitatively, it does not seem difficult to understand this relationship if the interpretation of the tensile strength of a cellulose sample as suggested earlier in this section is used as a starting point. According to this explanation, orientation would favor the mutual overlapping of cellulose chains and cellulose crystallites and hence would tend to avoid the existence of any especially weak cross section which would lead to the rupture of the filament on the application of a comparatively low force.

[52] E. E. Berkley, *Textile Research*, **9**, 355 (1939).

[53] T. Kerr and I. W. Bailey, *J. Arnold Arboretum*, **15**, 327 (1938); **16**, 273 (1935).

In order to get a numerical insight into the connection between the stretching of a filament and its strength, two steps are indicated. The first is a consideration of the dependence of the orientation of a given sample upon the amount of stretching which the material has undergone, and the second concerns the dependence of tensile strength upon orientation.

Numerous and very interesting contributions have been made by Hermans, Kratky, and Platzek[54–58] to the first of these two problems. Working with cellulose and cellulose xanthate at different degrees of swelling, these investigators have shown that each given sample behaves as if it were a mixture of two extreme cases, the behavior of each of which can be at least approximately described with the aid of mathematical analysis.

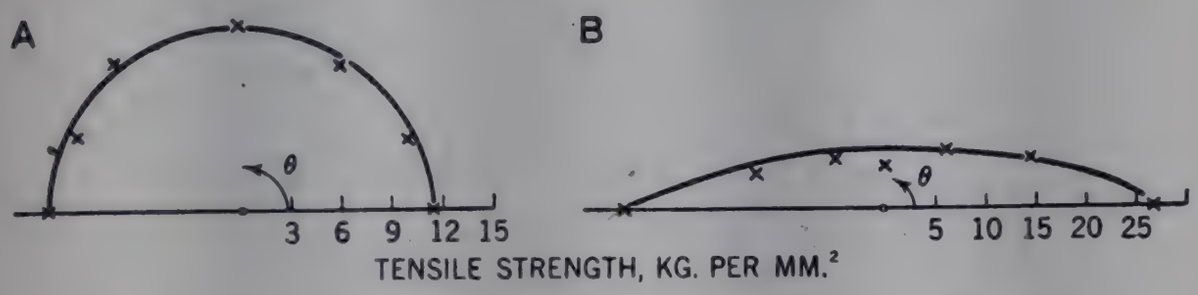

FIG. 65.—TENSILE STRENGTH DIAGRAM OF CELLOPHANE (MARK[17]).

A—Normal.

B—Stretched (oriented).

θ = Angle between direction of stretching and direction of applied stress.

The first case is represented by rigid, rodlike particles of a definite axis ratio which float in a viscous liquid (Fig. 66A). If such a system is stretched, the liquid flows and this flow causes the elongated particles to become more parallel. With this model, the number of rods (in the case of the cellulose, the number of crystallites) which occupy one certain angle to the direction of the stress can be expressed as a function of the elongation, with the aid of the following equation:

$$N_\alpha = N_0 \frac{v^3}{[1 + (v^3 - 1) \sin^2 \alpha]^{3/2}} \qquad (7)$$

where N_α = number of crystallites whose long axis has an angle between

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[54] P. H. Hermans, O. Kratky, and P. Platzek, *Kolloid-Z.*, **86**, 245 (1939); **88**, 68 (1939); **89**, 345 (1939).

[55] P. H. Hermans, O. Kratky, and P. Platzek, *Kolloid-Z.*, **87**, 296 (1939).

[56] P. H. Hermans, *J. Phys. Chem.*, **45**, 827 (1941).

[57] O. Kratky, *Kolloid-Z.*, **64**, 213 (1933); **68**, 347 (1934); **70**, 14 (1935).

[58] O. Kratky and H. Mark, *Z. physik. Chem.*, **B36**, 129 (1937).

α and $(\alpha + d\alpha)$ from the fiber axis, N_0 = total number of crystallites, and $v = \dfrac{L + dL}{L}$ = relative elongation of the sample.

Curve 1 in Figure 67 gives a graphical representation of equation (7). It is seen that comparatively high elongations are required in such a system in order to achieve a certain amount of parallelization. Orientation is not easy. This can be explained by considering that the particles do not exert any direct influence on each other but are merely oriented and aligned by the flow of the viscous medium in which they are embedded.

FIG. 66.—SIMPLIFIED PICTURES OF ELASTIC AND VISCOUS ELEMENTS IN A CELLULOSE FIBER.

A—Rigid crystallites imbedded in a viscous (amorphous) area.
B—Network of intermicellar (elastic) cellulose chains.

The other extreme case is represented by a network of elongated particles, such as crystallites or bundles of chain molecules, which are connected by flexible joints. Figure 66B is an attempt at presenting a schematic picture of this case. If the ends of such a system are pulled, the rods (in the case of cellulose, the crystallites) become parallel, since they have free rotation at the joints.

Here also, Hermans and Kratky[54, 55, 57] succeeded in deriving a mathematical expression for the amount of orientation produced by a given elongation. The relationship is the following:

$$N_\alpha = N_0 e^{2\tau} \left[1 + \tan^2 \frac{\alpha}{2}\right]^2 \left[1 + e^{2\tau} \tan^2 \frac{\alpha}{2}\right]^{-1/2} \tag{8}$$

where τ is defined by the equation

$$v = [\sinh 2\tau - 2\tau + 2 \ln \cosh \tau][\sinh \tau]^2 \tag{9}$$

Curve 2 in Figure 67 is a graphical expression of equations (8) and (9). In this extreme case the sample is seen to be much more susceptible to

orientation than before. The curve rises quite steeply, and reaches complete orientation at an elongation as low as 100%.

According to the theory, each actual fiber or film of cellulose or its derivatives behaves as if it were a mixture of the two extreme cases discussed above. Samples in a highly swollen state will approach more the behavior of Curve 1, while dry samples will approach Curve 2. Hermans[54, 55] and Kratky[57] have shown that this is actually the case. They have measured the orientation of the crystallites with x-rays, with the anisotropy of swell-

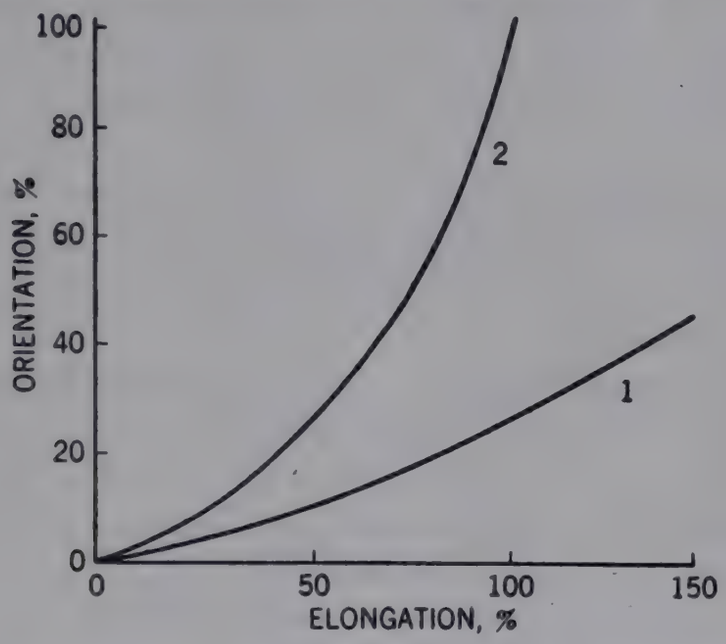

FIG. 67.—ORIENTATION OF CRYSTALLITES PRODUCED BY ELONGATION.

Curves:

1. Graph of equation based on picture given in Fig. 66A.
2. Graph of equation based on picture given in Fig. 66B.

ing, and with the aid of birefringence. In all cases, a relation between orientation and elongation is observed which can be interpreted as being intermediate between the two curves in Figure 67.

From the point of view of molecular interpretation, it may be reasonable to assume that each given sample of a high polymer is built up of some crystallized material, while the rest is in a state which can well be called amorphous. If these amorphous parts are abundant and highly swollen by a solvent or plasticizer, they will play the role of a viscous liquid in which the crystals are embedded, and the material approaches the theoretical one represented by Curve 1. If, on the other hand, the crystalline material is in excess so that chains may go from one crystal through an amorphous area to another crystal, then the amorphous areas in the sample

will do no more than play the role of flexible joints between the crystallites, and the other extreme will be approached.

Thus it seems that the connection between elongation and orientation in cellulose samples can be worked out with a numerical approximation which is not in too bad agreement with the experimental data. The other step, namely, to relate orientation quantitatively with tenacity, has been attempted by Mark.[28] He used the concept of rupture through the slipping of chains and showed that improved orientation makes it necessary to overcome the van der Waals' forces over a less smooth and hence enlarged area. It therefore increases the tenacity. However, it must be pointed out that these considerations are still in a preliminary and unsatisfactory state.

In summary, it may be said that orientation is a very important feature affecting the mechanical properties of cellulose and cellulose derivatives. Its influence can be understood reasonably well with the aid of the chain model of these substances.

Crystallization. It has already been mentioned earlier in the chapter that the chemical nature of chain molecules affects to a large degree their tendency to crystallize, and it may be appropriate to add a few more remarks about the importance of crystallization on the mechanical properties. It has been pointed out by various authors[28, 56, 59–62] that many experimental facts indicate that high polymers in general, and cellulose in particular, are built up of crystallized and amorphous portions. These portions may be oriented or unoriented and they may vary quite considerably as to their relative amount. High degrees of crystallization lead to materials having high moduli of elasticity (above 10^{11} dynes per cm.^{2}), high tenacities (above 4 g. per denier), but low elongations to break (below 8%), and poor transverse properties such as modulus of shear or bending strength. On the other hand, highly amorphous, unoriented samples show low moduli of elasticity (10^9 to 10^{10} dynes per cm.^{2}), low tenacities (below 1.5 g. per denier), but high elongations (above 25%), and improved bending strength.

It seems, therefore, that crystallization plays an important role, and that in building up a sample which is expected to have certain mechanical properties, the tendency of the material to crystallize, as well as the tendency of the crystallites to be oriented, has to be taken into account.

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[59] C. S. Fuller, W. O. Baker, and N. R. Pape, *J. Am. Chem. Soc.*, **62**, 3275 (1940); **64**, 776 (1942).

[60] C. S. Fuller, *Chem. Revs.*, **26**, 143 (1940).

[61] S. D. Gelman and J. E. Field, *J. Applied Phys.*, **10**, 564 (1939).

[62] R. F. Nickerson, *Ind. Eng. Chem.*, **33**, 1022 (1941).

However, at present there is no quantitative knowledge of how the chemical structure of the chains influences their crystallization tendency, or of how crystallization can be increased or decreased by changing the experimental conditions.

It can be seen from this discussion that the mechanical properties of cellulose and its derivatives are influenced by many different factors, and that only little is known quantitatively how each of them affects the final result. This explains why, at present, the problem of producing an artificial filament or film of given properties is still in a highly empirical state. Fundamental concepts such as the ones which have been expressed here may have a certain value in giving a general idea how to attempt to produce certain effects, but they certainly will be insufficient to settle any experimental details in the technical production of fibers or films. This still is left to a careful empirical study of all factors involved and still more, perhaps, to the personal experience and intuition of the experimenter.

2. Mechanical Properties of Cellulose Filaments and Films

H. MARK

The different tests which characterize the mechanical behavior of cellulose samples such as rayon, cellophane, and molded plastics may be divided into two groups: (1) those which follow very closely the practical use of the material and aim at a purely empirical characterization of the sample for some special purpose,[1, 2, 3] and (2) those which carry out a scientific experiment with the specimen. The latter aim at the determination of a fundamental quantity and at the correlation of that quantity with the molecular and supermolecular structure of the substance.[4–11]

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[1] H. Mark, *Die Physik und Chemie der Cellulose.* J. Springer, Berlin, 1932.

[2] O. Schmidhauser, *Melliand Textilber.*, **17**, 905 (1936).

[3] W. Weltzien and K. Götze, *Chemische und physikalische Technologie der Kunstseiden.* Akademische Verlagsgesellschaft m. b. H., Leipzig, 1930.

[4] K. Bennewitz and H. Roetger, *Physik. Z.*, **40**, 416 (1939).

[5] W. G. Burgers and J. M. Burgers, *First Report on Viscosity and Plasticity.* 2nd ed., Nordeman, New York, 1938.

[6] R. Houwink, *Elasticity, Plasticity and Structure of Matter.* University Press, Cambridge, 1937.

[7] E. Jenckel and W. Holzmüller, *Z. physik. Chem.*, **A186**, 359 (1940).

[8] S. S. Kistler, *J. Applied Phys.*, **11**, 769 (1940).

[9] K. H. Meyer, *High Polymers*, Vol. IV, *Natural and Synthetic High Polymers.* Interscience, New York, 1942.

[10] F. T. Peirce, *J. Textile Inst.*, **17**, T355 (1926).

[11] I. Sakurada, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 252 (1938).

A very large number of tests of the first kind, such as crease resistance liveliness, folding, and tumbling exist, but it would be outside of the scop of this presentation to enumerate and discuss these methods and the sig nificance of the results obtained through them. However, it must be em phasized that such tests are of great importance for the development o special qualities and for the achievement of technical successes. The selection and use of these tests require considerable experimental skill, and the evaluation of the results requires an equal amount of caution and criticism; it would be a difficult task to include them in this short treatise.

The tests of the second kind are the ones which will be described briefly in this section. It seems desirable to divide them into two classes: fiber tests and film tests.

(*a*) *Fundamentals of Mechanical Testing of Fibers*

The usual way to get an insight into the mechanical properties of a fiber is to examine its so-called stress-strain curve. As these curves are usually made, they do not really represent stress-strain relationships, but are, rather, load-elongation curves.

If a single fiber, such as ramie, cotton, or rayon, or a bundle of such fibers, with length l_0 and crosss ection q is fastened at one end and a force p is made to act on the other, the material elongates. A plot of the elongation Δl as a function of the force p gives the load-elongation curve, represented by equation (1).

$$\Delta l = \mathrm{F}(p) \tag{1}$$

Since Δl is always proportional to the original length l_0, equation (1) becomes

$$\frac{\Delta l}{l_0} = \mathrm{f}(\sigma) \tag{2}$$

where σ, the tension (stress), is defined as p/q (force per unit area). The right side of equation (2), $\mathrm{f}(\sigma)$, is a pure number, and the left side, $\Delta l/l_0$, is the strain, that is, the relative elongation (usually measured in per cent of l_0). The most general way to express the strain as a function of the stress is

$$\frac{\Delta l}{l_0} = \epsilon = a + b\sigma + c\sigma^2 + \ldots\ldots \tag{3}$$

It follows immediately that $a = 0$, because ϵ has to vanish if σ is zero. Hence

$$\epsilon = b\sigma + c\sigma^2 + \ldots\ldots \tag{4}$$

At sufficiently small stresses, all terms will be negligible compared with the first, and equation (5) is obtained:

$$\epsilon = b\sigma \tag{5}$$

It often happens at small stresses that ϵ disappears completely as soon as the external force is removed, so that the extension is perfectly elastic. In such cases, the stress-strain relationship represented by equation (5) is called Hooke's Law, and the reciprocal of b is called the modulus of elasticity E of the material. It has the dimension of dynes per cm.^{2} and measures

TABLE 1

MODULI OF ELASTICITY (E) OF VARIOUS FIBERS AND FILMS (CF., E. G., K. H. MEYER[9])

Substance	Modulus of elasticity, dynes per cm.^{2} $\times 10^{10}$
Crude linen, bone-dry	Up to 108
Crude hemp, bone-dry	Up to 70
Crude ramie, bone-dry	Up to 60
Crude ramie, air-dry (65% R.H.)	51
Highly stretched viscose rayon, bone-dry	45
Highly stretched viscose rayon, air-dry	33
Normal viscose rayon, bone-dry	14.7
Normal viscose rayon at −50°C.	15.7
Normal viscose rayon, air-dry	11.5
Normal viscose rayon, wet	1.32
Cotton, bone-dry	7–8
Cotton, air-dry	5.9
Acetate rayon, air-dry	6.1
Acetate rayon, wet	1.72
Silk, air-dry	14.4
Nylon (50% R.H.)	3.1
Cellophane	10.4
Cellulose nitrate film	5.0
Cellulose acetate film	4.07

the tension necessary to elongate the material by 100% under the assumption that equation (5) holds over this whole range of elongation. The amount of proportional elasticity for cellulose and its derivatives is, however, only a few per cent. Table 1 shows the moduli of elasticity for various fibers and films.

With the elongation Δl, there is always observed a transverse contraction $-\Delta q$ which, at small values of σ, is also proportional to the tension:

$$-\Delta q = b'\sigma \tag{6}$$

The constant b' is inversely proportional to E and measured by the Poisson ratio m:

$$b' = \frac{1}{mE} \tag{7}$$

If the density of the material remains unchanged during the experiment, m assumes the value $^1/_2$; if m is smaller, the material contracts; if it is larger, the material expands. Table 2 shows a few Poisson ratios for different materials.[1, 6]

Modulus of elasticity and Poisson ratio are the two quantities necessary and sufficient to characterize a material within the range of Hooke's Law.

TABLE 2

POISSON'S RATIOS FOR VARIOUS MATERIALS

Substance	Poisson's ratio
Steel	0.265
Copper	0.355
Lead	0.400
Glass	0.245
Ebonite	0.390
Rubber	0.490
Polystyrene	0.485
Gelatin	0.500

Outside of this range, the conditions become rather complicated. The stress-strain curve for cellulose samples assumes the general shape shown in Figure 68, and, if the different points of this curve represent true equilibrium positions (which can be maintained indefinitely), the differential quotient $d\sigma/d\epsilon$ can be used to describe the behavior of the material. If $d\sigma/d\epsilon$ is constant, the resistance of the sample against stress remains constant; if $d\sigma/d\epsilon$ increases, increasing stress is needed to produce the same additional elongation; that is, the substance reinforces itself, and the curve bends toward the ordinate. If, on the other hand, the curve bends toward the abscissa, it means that the internal structure of the material is weakened, as smaller $d\sigma$ values produce the same $d\epsilon$ as before. Hence $d\sigma/d\epsilon$ represents the resistivity of the sample against deformation. It can be described by the higher coefficients of equation (4).

A further complication in stress-strain curves is that the elongation, or at least a certain part of it, does not disappear immediately upon removal of the external stress. The behavior of different materials, especially of fibers, in this range becomes dependent upon various experimental condi-

tions, particularly upon time. Therefore, ϵ is not a function of σ alone, but of tension σ and time t:

$$\epsilon = f(\sigma, t) \tag{8}$$

Equation (8) shows that the stress-strain curve as such, without exact indications about the rate of loading, somewhat loses its significance, and a more detailed analysis has to be made.

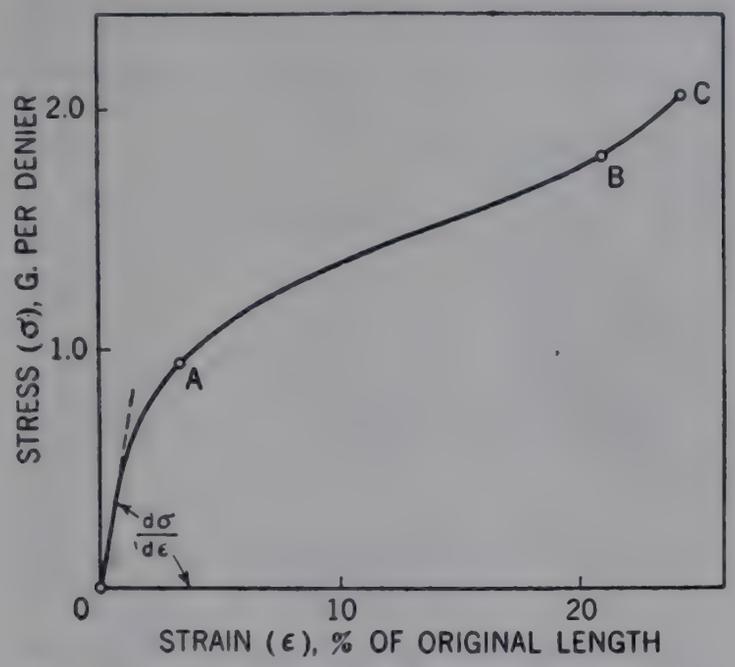

FIG. 68.—TYPICAL STRESS-STRAIN CURVE OF A CELLULOSE FIBER.

See pp. 1034–35 for further discussion of this curve.

(b) *Flow and Relaxation Tests*

Such studies have been made by many authors[3, 6, 12–20] and are usually carried out according to the following considerations. The time variable of equation (8) can be split conveniently into two simpler relationships: the *flow curve*, with ϵ a function of t at constant tension; and the *relaxation curve*, with σ a function of t at constant strain.

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[12] T. Barratt, *Trans. Faraday Soc.*, **20**, 279 (1924).
[13] R. H. Bellinson, *Textile Research*, **10**, 287, 316, 372 (1940).
[14] E. E. Berkley, *Textile Research*, **9**, 355 (1939).
[15] G. F. Davidson, *J. Textile Inst.*, **31**, T81 (1940).
[16] H. deWitt Smith and R. Eisenschitz, *J. Textile Inst.*, **22**, T158, T170 (1931).
[17] J. Karger and E. Schmid, *Z. tech. Physik.*, **6**, 124 (1923).
[18] H. Leaderman, *Textile Research*, **11**, 171 (1941); cf. also paper presented at the Am. Chem. Soc. meeting at Buffalo, Sept. 7–11, 1942.
[19] H. Mark, *J. Phys. Chem.*, **44**, 764 (1940).
[20] K. R. Fox and E. R. Schwarz, *Textile Research*, **12**, No. 10, 2 (1942).

Flow Curves. Flow curves of cellulose and its derivatives have been frequently measured,[8, 17, 18, 21–23] and a recent careful study by Leaderman[18] and Press[24] is especially noteworthy. The general shape of the curve is shown in Figure 69 for cotton (Curve 1), for normal (moderately stretched) viscose rayon (Curve 2), for acetate rayon (Curve 3), and for cellulose butyrate (Curve 4).

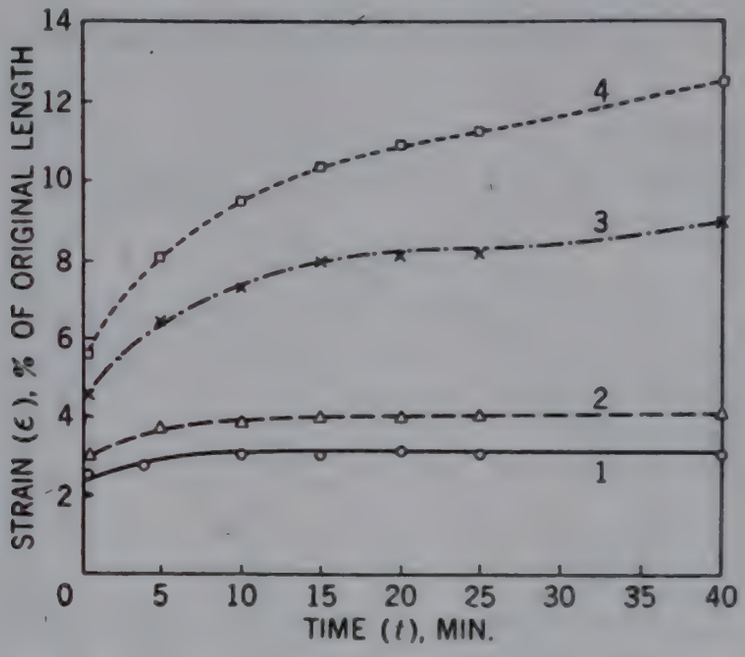

FIG. 69.—TYPICAL FLOW CURVES OF FIBERS OF CELLULOSE AND ITS DERIVATIVES.

Curves:

1. Cotton.
2. Viscose.
3. Acetate.
4. Butyrate.

It may be added that this type of flow curve is characteristic not only for cellulose, but for a large number of high-molecular-weight compounds, including inorganic systems such as cement and glass. Its main feature seems to be that three types of deformation are observed. These start to overlap each other as soon as an external force (stress or shear) is applied to the sample. The first is an instantaneous displacement which also instantaneously disappears as soon as the external force is removed. The

[21] E. C. Bingham, *Fluidity and Plasticity*. McGraw-Hill, New York, 1922.

[22] M. Harris, L. R. Mizell, and L. Fourt, *J. Research Natl. Bur. Standards*, **29**, 73 (1942).

[23] P. H. Hermans, *Kolloid-Z.*, **81**, 143 (1937); **83**, 71 (1938).

[24] J. Press, Thesis, Polytechnic Institute of Brooklyn, 1943; paper presented at the meeting of the Society of Rheology, Oct., 1942; *Rheol. Bull.*, **13**, No. 3, 7 (1942).

econd is a slow strain which completely vanishes equally slowly after the emoval of the external stress, and the last is a permanent deformation vhich does not disappear even after a long time following the removal of he external stress.

In order to get a clear insight into the prevailing conditions, a few well-nown but very fundamental facts and definitions[1, 3, 6, 9, 21, 25] should be eviewed briefly.

If a stress or shear is applied to any kind of material, two extreme cases f behavior are observed: in one of them the external force produces a

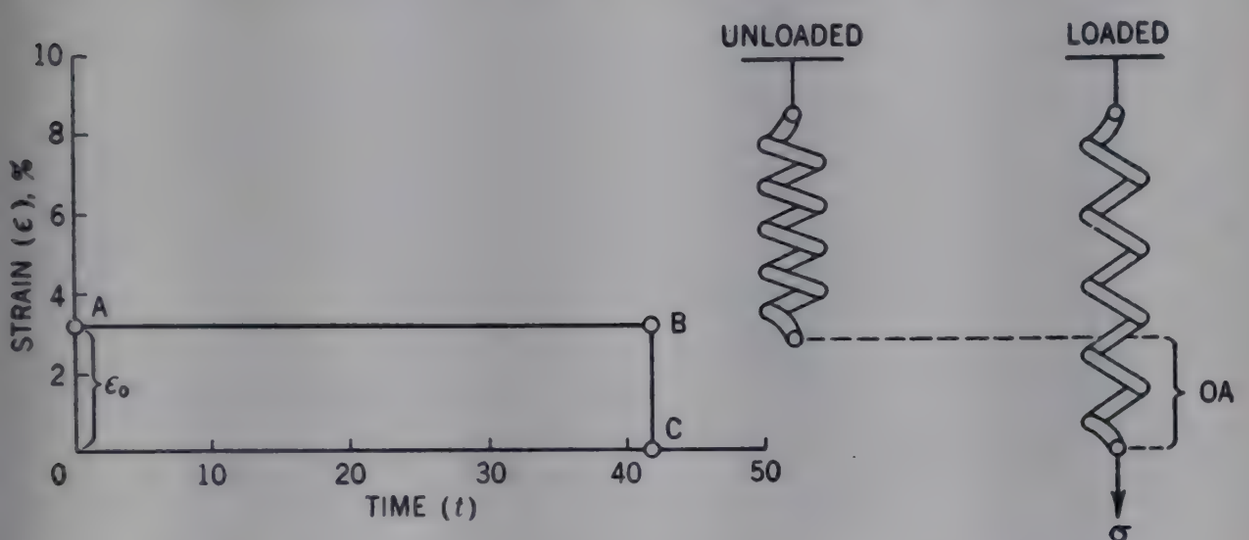

FIG. 70.—PURELY ELASTIC BEHAVIOR ACCORDING TO HOOKE'S LAW.
$\epsilon_0 = OA = CB = \sigma/E$, where E equals modulus of elasticity.

displacement, which disappears at once and completely, as soon as the material is unloaded. Such a system is called an *elastic solid*. Examples are platinum (and many other metals), quartz (and many other ionic crystals), and diamond. In the other extreme case, the external force produces a *velocity gradient*, which leads to a deformation through flow. This deformation remains indefinitely after the force ceases to act. Such a system is called a *liquid*. Examples are benzene, water, and mercury.

Figure 70 shows the flow curve of an elastic body. As soon as the stress or shear σ is applied, the deformation ϵ_0 takes place and remains constant as long as σ acts. If σ is removed, ϵ_0 disappears at once. Such a system may be conveniently idealized by a steel spring, shown also in Figure 70, and, according to the procedure usually adopted in the literature, is called an individual *elastic element*.

Figure 71 describes the behavior of a liquid. As soon as the external force

[25] M. Brillouin, *Ann. chim. phys.*, [7], **14**, 311 (1898).

(shear) σ is applied, flow sets in and the deformation increases proportionally with time. If the flow is stopped by removal of σ, ϵ keeps its final value ϵ indefinitely. Such a system may be represented by a piston which moves in a cylinder in which a liquid causes a certain friction (Fig. 71). This system is called an individual *viscous element*. Newton found that frequently the velocity gradient of the flow is proportional to the shear; the proportionality factor is called the *fluidity* ϕ, its reciprocal, the *viscosity* η of the liquid, and the whole phenomenon, *Newtonian flow*.

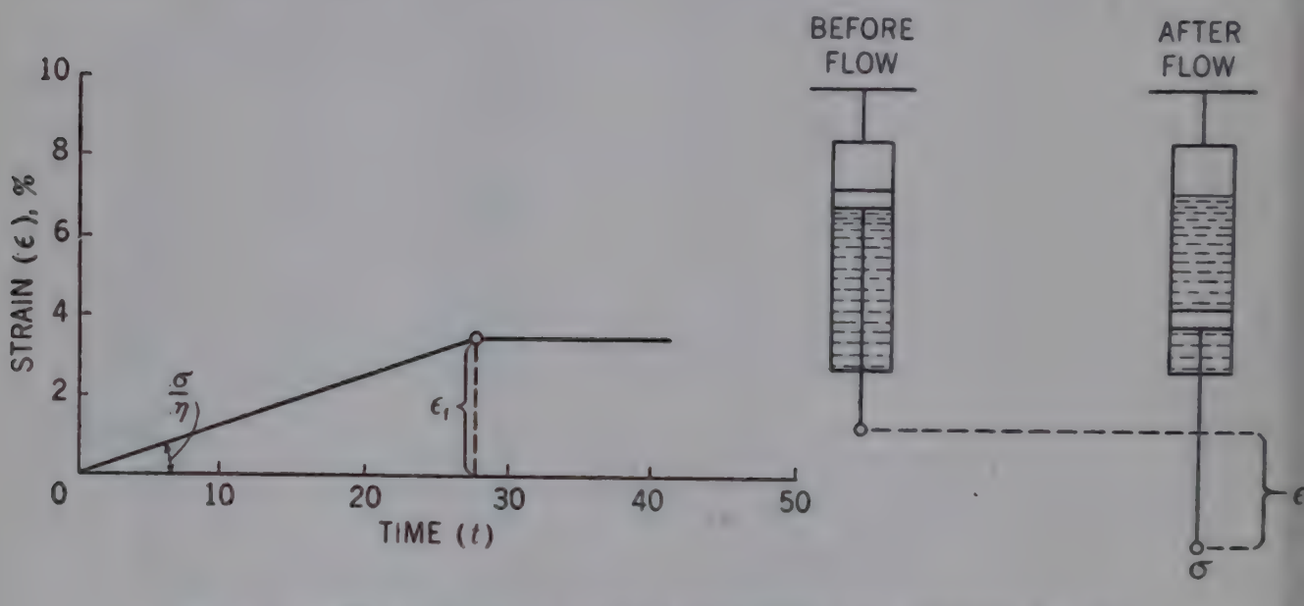

FIG. 71.—PURELY LIQUID FLOW ACCORDING TO NEWTON'S LAW.

$\epsilon_f = \frac{\sigma}{\eta} \cdot t = \phi \sigma t.$
σ = Shearing stress.
η = Viscosity of liquid.
ϕ = Fluidity of liquid.

Cellulose and its derivatives usually behave in a much less simple manner than do elastic solids or Newtonian liquids. In order to describe their properties, it seems convenient to build up gradually more and more complicated cases combining the elastic elements of Figure 70 and the viscous elements of Figure 71. This combination can be done by arranging these elements either in series or parallel. Maxwell[6, 26] was the first to investigate such combinations.

Figure 72 shows the arrangement in series. Both elements are subjected to the same stress; the total deformation is given by the addition of the individual deformations. If the load is applied, a sudden deformation ϵ_0 takes place, the magnitude of which is given by the modulus of the

[26] J. C. Maxwell, *Phil. Mag.*, [IV], **35**, 134 (1868).

elastic element. Then flow sets in and leads to an increase of ϵ proportional to time according to the fluidity (or viscosity) of the viscous element. If the load is removed, the spring jumps back immediately from B to C, which is equal to OA, but the constant elongation DM, which was produced by the flow, stays on indefinitely. The material shows plasto-elasticity.

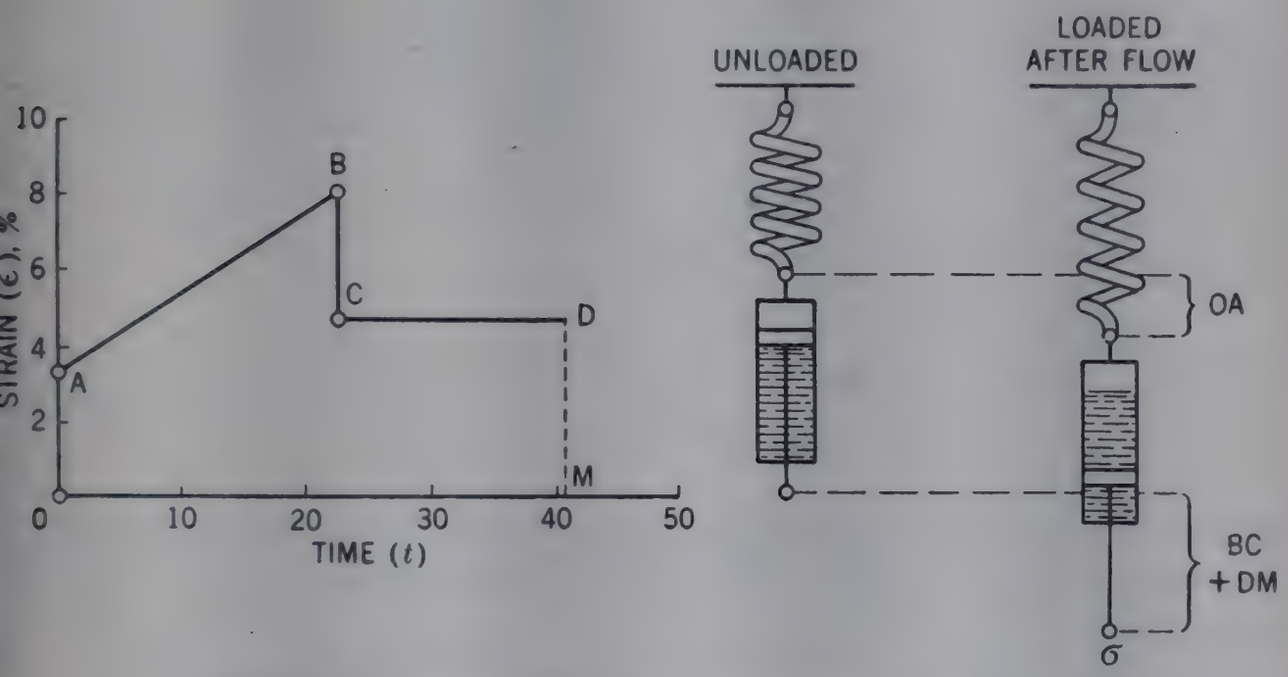

FIG. 72.—ELASTIC AND VISCOUS ELEMENTS IN SERIES.

$\epsilon = \epsilon_0 + \epsilon_f$.
$\epsilon_0 = OA = BC = \sigma/E =$ Ideal elastic deformation.
$\epsilon_f = DM = \phi\sigma t =$ Deformation due to flow.

Figure 73 shows the parallel arrangement of one viscous and one elastic element. Both elements have at any time the same elongation. In the first moment, if the system is loaded, the two elements (which we assume to have the same cross section) will have to stand the same stress. Under its influence, the spring starts to extend and the piston to flow. According to Hooke's Law, the stress which is taken up by the spring increases proportional to its elongation, and therefore less and less force is left to move the piston. Finally, all the stress is concentrated in the spring, and the piston stands still. The viscous element has gradually unloaded itself through flow, and has shifted the stress to the spring, which at the end of the experiment bears the whole load. Under the simple conditions of the example, ϵ increases exponentially with time (compare Fig. 73), just as in the case of the formation of a chemical compound or a radioactive element

by a first-order reaction rate. If the load is removed, the elastic energy which is stored in the extended spring gets to work and gradually moves the piston back into its original position, which, however, is reached only asymptotically. A retarded elastic recovery, which gives a straight line

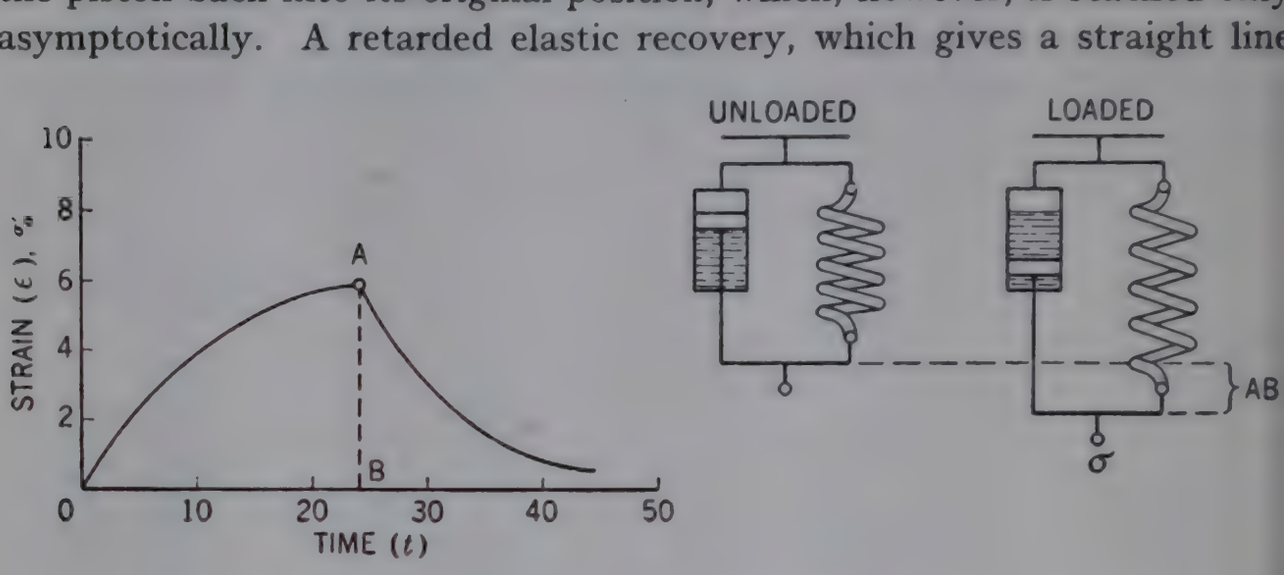

FIG. 73.—ELASTIC AND VISCOUS ELEMENTS IN PARALLEL.

$$\epsilon = \epsilon_2(1 - e^{-\phi_2 E_2 t}); \text{ where } \epsilon_2 = \frac{\phi_2}{E_2}.$$

for log ϵ as a function of time, is obtained. The slope of the straight line is a measure of the retarding action due to the viscosity of the damping piston.

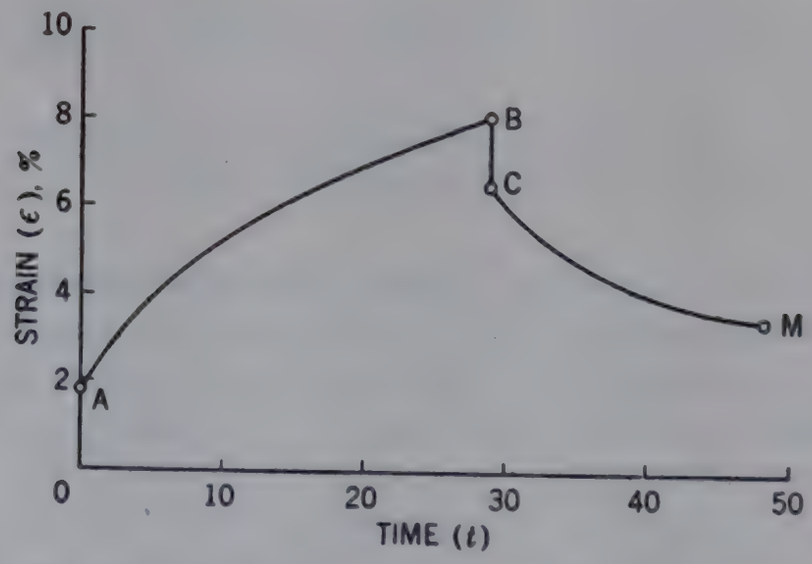

FIG. 74.—FLOW CURVE OF TYPICAL HIGH POLYMER.

However, even the two composite systems depicted in Figures 72 and 73 are not yet sufficient to represent the behavior of high polymers. They are only a step toward this goal. If a typical flow curve of a cellulose derivative (Fig. 74) is examined, it shows all the different elements of both cases

together, namely, a sudden jump, a retarded elastic extension, and a viscous flow.

The next approximation, therefore, leads to a system built up by two elastic and two viscous elements, having two different moduli E_1 and E_2 and two different viscosities η_1 and η_2 and being arranged parallel and in series, respectively. This case is shown in Figure 75; it has been frequently discussed in recent years, together with still more general systems, by many authors.[4–7, 18, 27]

The application of an external force immediately produces an extension of the upper (isolated) spring, as shown by ϵ_0 in the curve of Figure 75.

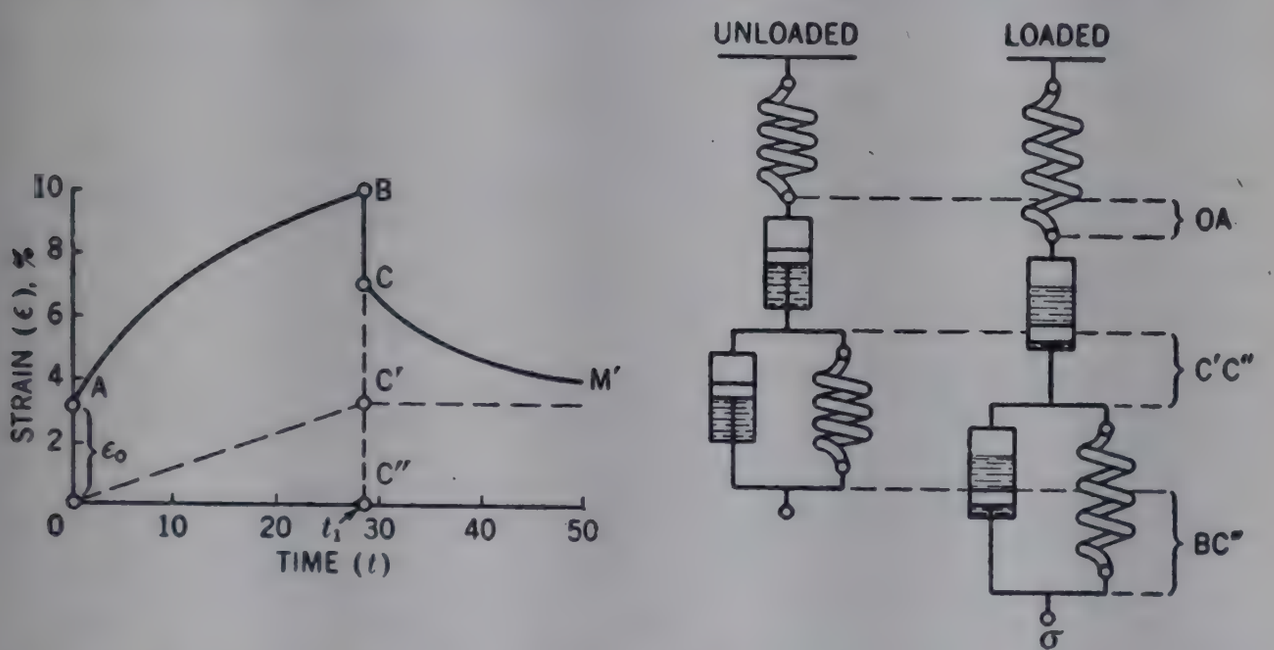

FIG. 75.—ELASTIC AND VISCOUS ELEMENTS COMBINED IN SERIES AND IN PARALLEL.

$$\epsilon = \frac{\sigma}{E_1} + \frac{\sigma}{\eta_1}t + \frac{\sigma}{E_2}\left(1 - e^{-\frac{E_2}{\eta_2}t}\right) = \epsilon_0 + \epsilon_f + \epsilon_2(1 - e^{-\phi_2 E_2 t}).$$

$\epsilon_0 = OA = BC$ = Ideal elastic deformation.

$\phi_1 \sigma t = C'C''$ = Viscous flow.

$\epsilon_2(1 - e^{-\phi_2 E_2 t}) = CC'$ = Retarded elastic deformation.

Simultaneously, the piston just below (isolated viscous element) starts to flow with constant velocity proportional to σ/η_1. The other piston also starts; at first the velocity is σ/η_2, but it decreases asymptotically to zero, due to the fact that the stress is gradually transferred from the flowing piston to the extending spring. A reinforcement along the line AB takes place. If, at the instant t_1, the load is taken away, then the isolated elastic element at once will contract an amount OA. This is represented

[27] N. W. Taylor, *Rheol. Bull.*, 12, No. 3, 27 (1941).

in Figure 75 by the distance BC. The piston below it does not mov
The lower spring, however, starts contracting with a velocity that decrease
to zero exponentially due to the damping action of the viscous elemer
arranged in parallel with it, allowing the system to approach asymptoticall
the line $C'M'$. The system thus exhibits ideal and retarded elasticit
back and forth, and true viscous flow. The curve in Figure 75, which show
its behavior graphically, resembles fairly well the type of experimenta
curves represented in Figure 74, and it may, therefore, be appropriate t
use it in taking the next step toward approximating the deformation c
high-polymeric materials.

The molecular significance of these stress-strain curves is, presumably
that in such systems as cellulose and its derivatives, elastic elements suc
as curled up chain molecules or clusters of them (which exhibit kineti
elasticity or Mack elasticity[28]) can be present in two different extreme situa
tions: first, extension does not involve the plastic displacement of any ac
jacent volume unit of the sample (for example, orientation of a crystallit
or flow inside of an amorphous area containing chain ends); second, ex
tension is possible only if such a process of rearrangement takes place, du
to the fact that the elastic element is somehow connected with its su
roundings by chains connecting the crystalline and amorphous areas, b
cross-links, or by intermolecular forces.

Two extreme types of viscous elements are also possible: first, thos
such that their flow does not stress any elastic element in the immediat
neighborhood (isolated viscous elements which lead to flow); and secon
those such that they can flow only if an adjacent volume unit is stresse
and stores up elastic energy (combined or connected viscous elemen
which show retarded recovery).

In reality, all sorts of intermediate cases, such as elastic elements havin
different degrees of coupling with viscous ones, can be expected to occu
Furthermore, it is probable, too, that more than two moduli of elasticit
and two viscosities will be necessary to describe the sample. In such a cas
a frequency distribution curve for both would be expected. Such a ge
eralization would be analogous to the procedure of Fuoss and Kirkwood,
who very successfully explained the electrical behavior of certain hig
polymers by assuming that a variety of dipoles of different magnitude an
different times of relaxation is responsible for the electrical properties.

However, as there are only a few measurements available on flow curv
of cellulose and its derivatives, it may be sufficient at present to confir

[28] H. Mark, *Ind. Eng. Chem.*, **34**, 449 (1942).
[29] R. M. Fuoss and J. G. Kirkwood, *J. Am. Chem. Soc.*, **63**, 385 (1941).

he discussion to the evaluation of them with the aid of two elastic and two iscous elements as indicated above. In this simplified case, the elongation ϵ as a function of time is given by the equation

$$\epsilon = \epsilon_0 + \epsilon_f t + \epsilon_2(1 - e^{-\phi_2 E_2 t}) \tag{9}$$

Here ϵ_0 represents the ideally elastic elongation and determines the modulus f the isolated elasticity according to the formula

$$E_1 = \frac{\sigma}{\epsilon_0} \tag{10}$$

The quantity ϵ_f accounts for the flow and determines the time of relaxation τ) of the isolated viscous elements according to

$$\tau_1 = \frac{\sigma}{E_1 \epsilon_f} t \tag{11}$$

This time of relaxation can be converted into the viscosity by means of

$$\eta_1 = E_1 \tau_1 \tag{12}$$

It is of importance to point out that these two characteristic constants or the isolated elasticity and viscosity can be directly and independently letermined by measurements at very short times, such as sound velocity nd rebound (see Section G, 1 of this chapter), and at very long times final linear flow of the sample).

The last term of equation (9) represents the exponential reinforcement. The two constants, ϵ_2 and ϕ_2, are directly connected with the modulus of he delayed elasticity and with the viscosity of the retarding viscous lements according to the following relationships:

$$E_2 = \frac{\sigma}{\epsilon_2} \tag{13}$$

$$\frac{1}{\phi_2} = \eta_2 = E_2 \tau_2 \tag{14}$$

A plot of the log of $[\epsilon - \epsilon_0 - \epsilon_f t]$ against time gives a straight line if the whole reinforcement during the flow of the material is due to the distribution of stress as discussed above.

Recent experiments by Fourt,[30] Harris,[22] Press,[24] and Sookne[31] have shown that, in certain cases and over limited periods of time, the above

[30] L. Fourt, unpublished data; see also Harris and coworkers, ref. 22, p. 1020.

[31] A. M. Sookne, unpublished data; see also Harris and coworkers, ref. 22, p. 1020.

outlined analysis leads to agreement with experiment. In other cases, however, and over longer periods, a reinforcement which considerably exceeds the one predicted by equation (9) is observed. It has been suggested that this additional reinforcement can be explained by the assumption that the number of viscous and of elastic elements does not remain constant during the experiment, but that viscous elements disappear and are converted into elastic ones through additional crystallization and orientation while the sample is extended. It seems that the addition of a term of the form $\epsilon_3 \log t$ to equation (9) can express the influence of additional crystallization.

It can be seen from equation (9), which describes the flow at a given (constant) stress, that all terms are assumed to be proportional to the stress.

TABLE 3

ELASTIC MODULI FOR INSTANTANEOUS AND RETARDED ELASTICITY (PRESS[24])

Substance	Modulus for the instantaneous elasticity, dynes per cm.^{2} $\times 10^{10}$	Modulus for the retarded elasticity, dynes per cm.^{2} $\times 10^{10}$
Nylon, drawn	5.3	4.7
Wool	0.72	0.69
Wool	0.75	0.57

This assumption, of course, is not true under all conditions, particularly at high stresses, and hence equation (9) must be considered only a first approximation in the attempt to describe the flow of cellulose samples.

Table 3 shows a few values which have been obtained recently by Press.[24] It can be seen that the elastic moduli for the isolated and delayed elasticity are of a rather similar magnitude. This can be interpreted, perhaps, to mean that the same kind of arrangement of the cellulose chains produces both types of elastic elements, with the difference that sometimes they are less firmly connected with their surroundings (isolated units) and sometimes they are more closely united with their neighborhood.

The order of magnitude of the moduli corresponds to the modulus of the kinetic chain elasticity and of the van der Waals' forces,[11, 32, 33] showing that apparently the covalent bonds in the interior of the chains are not very much affected during these flow experiments. This fact can readily be understood from a consideration that the tensions applied were of the

[32] T. Alfrey and H. Mark, *Rubber Chem. and Tech.*, **14**, 525 (1941).
[33] K. H. Meyer and W. Lotmar, *Helv. Chim. Acta*, **19**, 68 (1936).

order of magnitude of only 1 g. per denier, which corresponds to 10^9 dynes per cm.^{2} (compare the discussion in Section G, 1 of this chapter).

Similarly, it turned out that the viscosities of the isolated and combined flow are of the order of magnitude of 10^7 to 10^9 poises, just as would be expected for the flow of such rigid structures. However, there is, at present, not enough experimental material available to enter into a more thorough discussion of the significance of such measurements.

Relaxation Curves. The relaxation of stress in a given sample at constant length can be considered from the same point of view as has just been done for elongation at constant stress. If a sample is stretched quickly to a certain length, energy is stored in it, and this energy will disappear as soon as the viscous elements in the material can act. If a viscous and an elastic element are connected in series and stretched to a certain length, potential energy will be stored in the spring. If the length is then kept constant, the viscous element starts to flow, and an exponential relaxation of the tension in the elastic element takes place according to equation (9). On the other hand, if a strain is present in a system in which viscous and elastic elements are connected in parallel, no such relaxation will take place.

Measurements of the relaxation of the tension at given elongation, therefore, provide an independent measure of the isolated elastic modulus and the isolated viscosity. Experiments of this type have been frequently carried out with materials such as glass or artificial resins,[8, 27, 34] but there are as yet no such measurements available on cellulose derivatives.

Flow curves and relaxation curves together describe the mechanical behavior of the material at a given tension or length as closely as can be expected by static experiments. They lead to the conception that viscous and elastic elements of various moduli and viscosities connected in parallel and in series determine the behavior of cellulose and cellulose-derivative samples. The experimental material at present is scarce, but it seems that the order of magnitude of the moduli and of the viscosities are in agreement with that expected from the molecular model.

In order to summarize this situation, Table 4 is presented here. It enumerates the different molecular elementary processes of elasticity and of flow, together with the characteristic qualities of each. In the case of elastic processes, the modulus, its temperature dependence, and the range of elastic extensibility are shown in Table 4A, together with an indication how the change of free energy during extension is affected by

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[34] S. L. Bass and T. A. Kauppi, *Ind. Eng. Chem.*, 29, 679 (1937).

TABLE 4

ELEMENTARY PROCESSES OF ELASTICITY AND FLOW

A. Elasticity

ΔF mainly affected by	Molecular mechanism involved	Modulus, dynes per sq. cm.	Range of elastic extensibility, %	Dependence upon absolute temperature	Typical example
ΔH	Extension of chemical main valence bonds	5×10^{11}–5×10^{12}	0.1–0.5	Slight and proportional to $1/T$	Ionic forces: rocksalt Metallic forces: tungsten Covalent forces: diamond
ΔH	Bending of covalent bonds	5×10^{10}–5×10^{11}	0.2–0.8	Slight and proportional to $1/T$	Diamond, quartz
ΔH	Extension of hydrogen bonds	5×10^{10}–5×10^{11}	0.2–0.8	Slight and proportional to $1/T$	Ice
ΔH	Extension of van der Waals' bonds	1×10^{10}–1×10^{11}	0.5–1.5	Slight and proportional to $1/T$	Cane sugar, phthalic anhydride, naphthalene
ΔS	Compression o an ideal gas	10^6 at 1 atm.	Infinite	Proportional to $\frac{R}{V} \cdot T$	Air
$\Delta H(s) + \Delta S(l)$	Extension of van der Waals' forces combined with kinetic elasticity of long-chain molecules	10^6–10^7	Up to 1000%	Proportional to T	Small forces: rubber, polybutadiene
$\Delta H(m) + \Delta S(m)$		10^7–10^8			Medium forces: polyesters, polyvinyl alcohol
$\Delta H(l) + \Delta S(m)$		10^8–10^9			Strong forces: cellulose, nylon, proteins

NOTE: $\Delta H(s)$ means that the contribution of this particular mechanism to the ΔH-form in the free energy change is slight; $\Delta H(m)$ means that it is moderate; and $\Delta H(l)$ means that it is large. The same also holds for $\Delta S(s)$, $\Delta S(m)$, and $\Delta S(l)$.

B. Flow

Moving element	Average volume, Å^3	Average energy of activation, cal. per moving element	Viscosity at melting point, poises	Time of relaxation, seconds	Typical example
Single atoms	10	1000	10^{-3}	10^{-13}	Argon
Single molecules:					
Small forces	...	2000	10^{-2}	10^{-12}	Pentane
Medium forces	50–500	3–4000	10^{-1}–1	10^{-11}–10^{-10}	Acetaldehyde
Strong forces	...	4–6000	1–10	10^{-10}–10^{-9}	Octyl alcohol
Aggregates of molecules	10^2–10^4	10,000	10–10^2	10^{-8}–10^{-6}	Glycerol
Segments of macromolecules	10^2–10^4	20–40,000	10^3–10^5	10^{-7}–10^{-5}	Vinyl polymers
Aggregates of macromolecules	10^5–10^8	above 100,000	above 10^5	above 10^{-5}	Cellulose esters

each individual process. In the case of viscous processes, the average volume of the moving particle, its activation energy, its viscosity, and the corresponding time of relaxation are contained in Table 4B.

It can be seen that, in both cases, elasticity and viscosity, a considerable number of elementary processes can occur, and it is therefore not surprising that their superposition leads to a rather complex behavior. It seems to be characteristic of high polymers that more than one of the elementary processes as listed in Table 4 are cooperating to build up the mechanical properties of the macroscopic sample.

(c) *The Stress-Strain Curve*

For practical purposes, however, stress-strain, or, more exactly, load-elongation curves are usually and even exclusively used. Although they do not give information as to the fundamental tensile properties of the sample, they are very useful in obtaining relative values for comparing different products under identical conditions. This, of course, is the main purpose of all practical fiber testing, in which the load-elongation curve plays a paramount role. However, from the fact that any cellulose sample acts as if it were built up by elastic and viscous elements, it would be expected that the load-elongation curve would depend in a rather complicated manner upon various experimental conditions.

Experimental Factors Influencing the Shape of the Stress-Strain Curve. The most important of the experimental conditions are the rate of loading,[1, 6, 18, 21] the humidity of the atmosphere or the presence of other swelling agents,[1, 9, 13, 35] and other factors which weaken the filaments during the experiment or which are connected with its natural nonuniformity.[1, 10, 13, 36–38]

Rate of Loading. This has already been discussed in the preceding paragraphs. The conclusion arrived at was that a reliable and thorough description of the material can only be obtained with the aid of flow and relaxation curves.

In normal fiber testing, however, experience has shown that a certain rate of loading leads to reproducible and useful load-elongation curves which reflect at least some of the technical properties of the fiber in a satisfactory way. Obviously, the more viscous elements a given specimen

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[35] K. C. Brown, J. C. Mann, and F. T. Peirce, *J. Textile Inst.*, **21**, T186 (1930).
[36] E. Midgley and F. T. Peirce, *J. Textile Inst.*, **17**, T305 (1926).
[37] F. T. Peirce, *J. Textile Inst.*, **17**, T355 (1926).
[38] F. T. Peirce and R. J. Stephenson, *J. Textile Inst.*, **17**, T645 (1926).

contains, the more pronounced will be the influence of the rate of loading on the shape of the curve. This is due to the fact that if the tension σ is increased in an arbitrary way, the viscous elements in the sample flow according to their viscosities and produce some reinforcement and some relaxation, so that the net effect of these superimposed rate processes is difficult to predict. Normally, the applied rate of loading is about 10^{-2} to 10^{-1} g. per denier per sec., corresponding to a rate of extension of 10^{-2} to 10^{-1}% per sec. As the elongation to break ranges between 5 and 30%, the duration of such extension experiments amounts to a few minutes. As such tests are very widely used in industry they must, of course, be not too clumsy or extended.

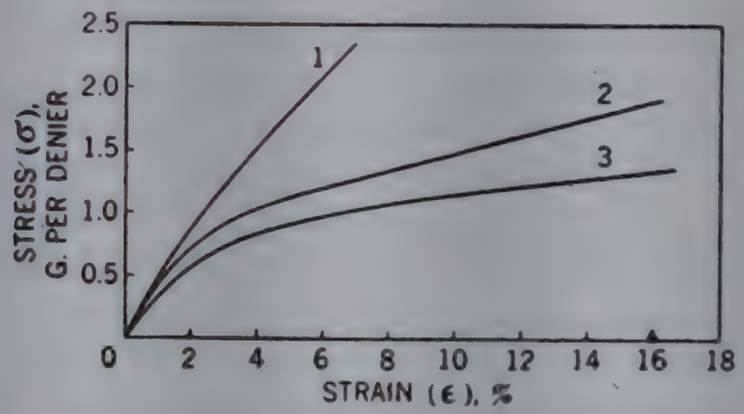

FIG. 76.—INFLUENCE OF THE RATE OF LOADING ON THE STRESS-STRAIN CURVE OF VISCOSE RAYON YARN.

Curves:

1. Very high rate of loading.
2. Normal rate of loading.
3. Very low rate of loading.

Figure 76 shows the stress-strain curve of a viscose rayon yarn at 65% relative humidity (R.H.) at a very high rate of loading (Curve 1), under normal conditions (Curve 2), and finally at a very low speed (Curve 3). As expected, the fibers show much more flow if the loading is very slow. The two extreme cases are the impact test, which amounts to loading the filaments up to their breaking strength within a few tenths of a second, and the flow curve carried out at a stress which is just sufficient to break the material. The impact strength of a filament is always higher than its limiting flow tenacity. Figure 77 shows a few flow curves of acetate rayon which are selected to demonstrate this fact. These flow curves are taken at different stresses, and it can be seen from Curve 1 that, after a comparatively short elongation, a new equilibrium is practically reached. This means that the filament will not stretch farther within the next

24 hours. This new equilibrium is due to the reinforcement which has been described above.

Curve 2 shows how a similar process takes place if a larger stress is applied. In this case, the material must elongate more than before in order to reach a sufficiently reinforced structure. This, presumably, means that more internal changes have to be accomplished in order to withstand the higher stress and to establish equilibrium.

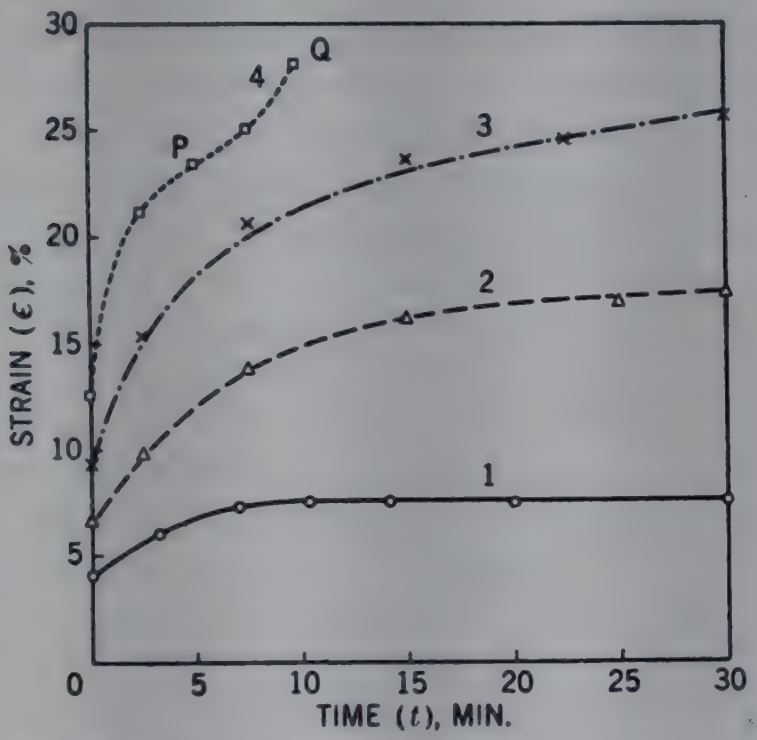

FIG. 77.—INFLUENCE OF APPLIED STRESS ON THE FLOW CURVE OF ACETATE RAYON.

Point P represents the time at which accelerated flow sets in and leads to break at Point Q.

Curves:

1. 0.5 g. per denier.
2. 0.8 g. per denier.
3. 1.2 g. per denier.
4. 1.4 g. per denier.

Curve 3 shows that the same happens even if one applies a tension of 1.2 g. per denier. However, as soon as the external force reaches that applied in Curve 4, the material first reinforces itself by the mechanism discussed above, but then another effect occurs. The tension increases due to the reduction of the cross section, and, at that moment (Point P in Curve 4), an accelerated flow sets in and leads to the break of the fiber. The tension which will just cause a break after being applied for an infinite time is called the *intrinsic tenacity*.

On the other hand, if the load is increased at a given finite rate, there will be an increase in tenacity (or tensile strength) over the minimum (intrinsic tenacity). In other words, a higher stress is necessary to break the filament than would be required if sufficient time were allowed for the material to flow. The difference between impact strength and intrinsic tenacity, therefore, will be larger, the higher the rate of loading and the slower the flow at the critical Point P.

Humidity and Swelling. The action of humidity and other swelling agents is very pronounced. This can be clearly seen in the influence of humidity on the shape of the stress-strain curve. Swelling accelerates the action of viscous elements. It lowers the yield point sometimes to such an extent that the flow starts immediately after loading begins, and it decreases the viscosity of the viscous elements considerably. Presumably, the molecules of the swelling agent enter the amorphous or mesomorphous portions of the sample and weaken the intermolecular bonds between the chains, thus facilitating any kind of irreversible displacement.

In practical fiber testing, the material is usually conditioned by bringing it into equilibrium with an atmosphere having 65% R.H. at 20–25°C. Stress-strain curves taken with such samples and with the rate of loading as mentioned above can be considered as corresponding to normal conditions.

Nonuniformity Factors. To rupture a fiber or a yarn in a testing machine without damaging it by clamping it at its ends is very difficult. Jaw breaks frequently occur, and it is questionable to what extent they are due to damaging of the fiber in the clamp. Although such considerations are very important for the statistical evaluation of the stress-strain curves, they lead too far into the technical domain of fiber testing to discuss them in this chapter. There is, however, an intrinsic nonuniformity in all fibers built up from cellulose and its derivatives. This nonuniformity is worthy of brief discussion because it concerns the material and the mechanisms by which the fiber has been produced. It has been deemed advisable to include this discussion in a separate section ((*d*) *Influence of Weak Spots*, p. 1035) of this chapter. The intrinsic nonuniformity does not so much affect the shape of the stress-strain curve point by point as it affects the point at which break occurs. In other words, it affects mainly the *tensile strength* and the *elongation to break*.[1, 36, 37, 39]

Significance of the Influence of Experimental Factors on Stress-Strain Curve. In the general shape of the load-elongation curves of cellulose and its derivatives as shown in Figures 68 and 76, three different sections can be distinguished.

[39] F. T. Peirce, *J. Textile Inst.*, **18**, T475 (1927); **20**, T133 (1929).

The first part of the curve is comparatively steep, showing that, under the influence of the external force, tension is built up rapidly in the sample. This, presumably, is due to the action of the elastic elements and is more pronounced, the higher the modulus and the greater the proportion of these elements.

In the neighborhood of Point A in Figure 68, the material starts to yield and considerably larger elongations are necessary in order to build up corresponding tensions than between *O* and *A*. Presumably, the viscous elements then take part in the elongation of the material. The Point A (which is not very sharply defined) is called the *yield point* of the investigated substance. It is, of course, dependent upon the rate of loading and upon various other experimental conditions such as those mentioned above.

While the material flows, the elastic elements are, of course, also active, and, even during flow, more elastic energy is accumulated in the sample. Sometimes, if the conditions are favorable for flow, it happens that the break occurs without any visible change in the shape of the curve, and the end point lies somewhere in the neighborhood of Point B on the curve in Figure 68. Sometimes, however—and this always seems to be a sign for crystallization during flow—the load-elongation curve bends again, and the tension rises rapidly until break occurs (Point C).

As a first approximation, it may therefore be assumed that the two sections, *OA* and *BC*, reflect mainly the action of elastic elements. The ones which produce *OA* have a low modulus and presumably develop either Mack elasticity or kinetic elasticity, due to van der Waals' forces and entropy changes, respectively. The elastic elements which produce *BC* have a much higher modulus, and presumably reflect the elasticity of the crystallized phase which is due to the action of chemical bonds (extending covalent bonds or bending them out of their natural direction).

(*d*) *Influence of Weak Spots*

All natural and synthetic fibers and yarns contain two types of nonuniformities: (1) single fibers, as well as spun and twisted yarns, exhibit different tenacities and elongations to break at different points along the length of the specimen; and (2) yarns, which are built up from fibers of different individual properties, will have variable tenacity and elongation over their cross section. According to what has been said above, it must be assumed that even single natural and synthetic fibers exhibit fluctuations in mechanical properties over the cross section, due to the fact that they can be considered to be built up of elements (fibrils) having different elastic and viscous behavior.

In both cases, the presence of weaker portions of the sample decreases in a statistical manner the average tenacity of the material, a factor which is of considerable importance in practical fiber testing.

These two types of nonuniformities may be restated as follows: first, there are weak spots distributed over the length of the fibers; and, second, there are weak spots distributed over the cross section of the fibers.

Weak Spots Distributed along the Fiber Length. If imperfections or flaws are irregularly distributed along a fiber or yarn, the tenacity is going to depend upon the length of the samples used for the tensile strength test.

A preliminary insight into the dependence of tenacity upon specimen length can be obtained as follows:

Let the shortest samples which still can be satisfactorily handled in the tester be considered as having a length l_0 (presumably somewhere around one inch) and an average tenacity t_{s_0}. If a filament having the length l and the tenacity t_s is now increased in length by dl, a decrease in tenacity $(-dt_s)$ must be expected. It seems reasonable to assume that this loss in tenacity will be given by

$$-dt_s = \alpha \frac{dl}{l} \tag{15}$$

The reason for this is that the probability of creating a new imperfection will be proportional to dl, while the chance of already having a weak spot in the sample is proportional to l. Hence, the probability of getting a weaker filament by increasing its length from l to $l + dl$ is proportional to the ratio $dl:l$; the coefficient α indicates the average frequency of flaws along the specimen and may be considered as a measure of imperfections in the material. Integration of equation (15) gives

$$t_{s_l} = t_{s_0} - \alpha \ln \frac{l}{l_0} \tag{16}$$

This equation shows that the observed tenacity (t_{s_l}) plotted against the logarithm of l/l_0 gives a straight line, whose intercept with the ordinate is the maximum obtainable or substance strength, while the slope offers a measure of the nonuniformity of the material.

There are a few experimental data available to check equation (16). Bellinson,[13] Mark,[1] and Peirce,[10, 36–39] have measured the tenacities of various fibers at different sample lengths, and it seems that their results are approximately in agreement with the requirements of equation (16). These measurements have shown that yarns of different source and of different technical history do show appreciable differences in α-values.

This method of estimating the uniformity of fibers or yarns is experi-

mentally and theoretically simple and is therefore widely used in practice. It is, however, only a very preliminary approximation. A much more thorough analysis has been carried out by Peirce and his coworkers.[10, 35–43]

If the tenacities are determined for a large number N_0 of fibers or yarns all having the length l_0 which corresponds to the shortest length that still can be satisfactorily handled, they obviously will not all be identical but will lie along a distribution curve giving the number dN of filaments having a tenacity between t_s and $t_s + dt_s$ as a function of t_s:

$$dN = \psi(t_s)dt_s \tag{17}$$

Such tenacity distribution curves have frequently been determined experimentally; they are usually not of the normal Gaussian type but exhibit a more or less pronounced skewness. The integral over the whole distribution curve from zero to infinity obviously gives the total number of filaments under consideration.

Hence:

$$\int_0^\infty \psi dt_s = N_0 \tag{18}$$

Furthermore, the probability that any given sample has a tenacity above t_s will be represented by

$$\int_{t_s}^\infty \psi dt_s \Big/ \int_0^\infty \psi dt_s = \frac{1}{N_0} \int_{t_s}^\infty \psi dt_s \tag{19}$$

The length of a specimen built up from n consecutive elements of the length l_0 will be nl_0, and the problem is to determine the tenacity of this sample as a function of n and of the distribution law, which characterizes its individual components of length l_0.

To produce a composite sample having a tenacity t_s, it is obviously necessary that one of its elements has this tenacity t_s, while all the others have higher strength. The probability that one of the n elements of our sample has a tenacity between t_s and $t_s + dt_s$ is $n\psi dt_s/N_0$ and that all other $(n-1)$ elements have higher strength is $\left[\int_{t_s}^\infty \psi dt_s/N_0\right]^{n-1}$.

Thus the chance of finding a composite sample having a tenacity between t_s and $t_s + dt_s$ is given by

$$\frac{1}{N_0^n} n\psi dt_s \left[\int_{t_s}^\infty \psi dt_s\right]^{n-1} = N(n, t_s) \quad \text{when} \quad N_0 \gg n > 1 \tag{20}$$

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[10] F. H. Clayton and F. T. Peirce, *J. Textile Inst.*, **20**, T315 (1929).
[41] G. G. Clegg and S. C. Harland, *J. Textile Inst.*, **14**, T489 (1923).
[42] G. E. Collins, *J. Textile Inst.*, **15**, T519 (1924).
[43] J. C. Mann, *J. Textile Inst.*, **18**, T253 (1927).

This is proportional to the number of samples of this tenacity, and hence equation (20) gives the tenacity distribution curve of samples having the length nl_0. In order to evaluate it numerically, the algebraic expression for $\psi(t_s)$ has to be known.

It has already been mentioned that generally $\psi(t_s)$ does not have the normal Gaussian form, but shows a certain skewness toward lower tenacities. There exists, however, no distribution curve for the substance strength of any cellulose fiber which would be sufficiently well established to be used

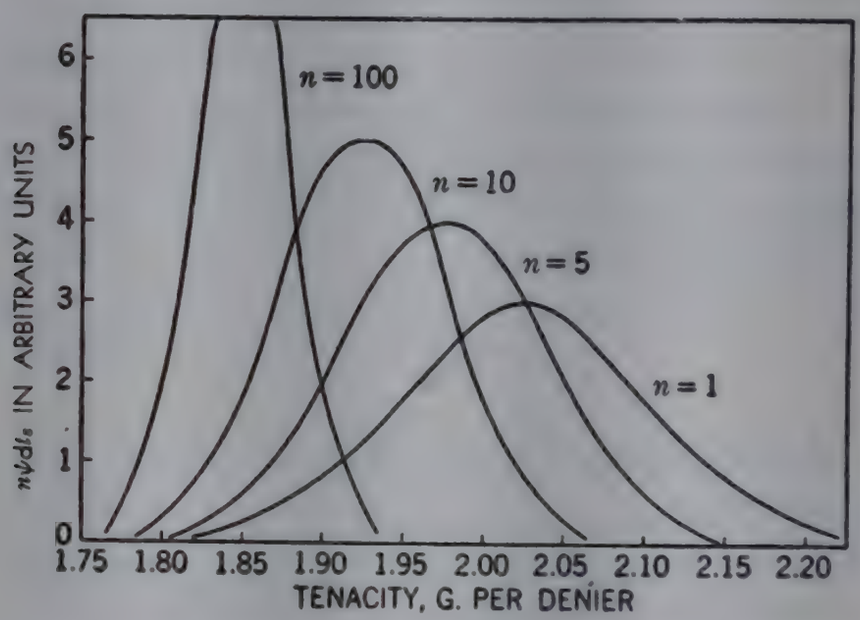

FIG. 78.—TENACITY DISTRIBUTION CURVES FOR NON-UNIFORM FIBERS OF VARIOUS LENGTHS.

n = Number of consecutive elements of length l_0 in each fiber.

as a reliable basis for the above computation. Therefore, Peirce[10] has used the error distribution function to show how the mean tenacities and the standard deviation are affected by the length of the sample:

$$\psi(t_s) = \frac{N_0}{\sqrt{2\pi s}} \exp\left[-\frac{1}{2s}(t_s - t_{sm})^2\right] \qquad (21)$$

where t_{sm} = mean tenacity, and s = standard deviation.

Figure 78 gives the result of his computation. It can be seen that increasing length shifts the maximum of the curves (mean or average tenacity) to lower values but makes the curves sharper (decreases standard deviation). This can easily be understood, because a larger number n of independent elements l_0 must increase the probability of having a very

weak link in the specimen, but (as usual in statistics) must decrease the fluctuations and hence increase the modulus of precision.

Thus, the investigation of samples with different lengths offers a very interesting means of obtaining information as to the homogeneity of a given fiber type.

Weak Spots Distributed over the Cross Section. It has already been mentioned that any sample—single filament, yarn, or film—must be expected to exhibit certain imperfections over its cross section. In the case of a yarn, this is due to the fact that the individual filaments will vary in strength and elongation to break. In the case of a single filament or film, a similar variation will be seen to be present by a consideration of the different elements dq of a certain cross section of height dh. Cotton has a hollow core and a dense primary and secondary cell wall; certain rayon fibers have a more or less pronounced skin formation. But even if there is no visible heterogeneous character of different parts of a given cross section, there may be a submicroscopic one due to the fact that a certain volume unit $dq_1 \cdot dh$ is occupied by a crystal, oriented parallel to the fiber axis, while another unit $dq_2 \cdot dh$ is filled with curled up and entangled chains. The first unit will have a high elastic modulus ($\sim 10^{11}$ dynes per cm.^{2}), high tenacity ($\sim$5 g. per denier), and a low elongation to break ($\sim$2%), while the other will have a low modulus ($\sim 10^9$ dynes per cm.^{2}) and a high elongation to break (perhaps up to 100%). Thus, even single fibers have to be considered as composite structures.[8, 19, 32]

For the following discussion, it will be assumed that the distribution function has the symmetrical Gaussian form[8] and that equation (18) represents the total number of all filaments or fibrils N_0. If all of these have the same individual cross section dq, then $N_0 dq$ is the cross section of the sample. With a load p_0 on this sample, the resulting stress[10, 39] will be

$$\sigma_0 = \frac{p_0}{dq \int_0^\infty \psi dt_s} = \frac{p_0}{N_0 dq} \tag{22}$$

From Figure 79, it is evident that, up to a load p_1, there will be only stretching of the individual fibers or fibrils, but no rupture. In this case, each single fiber has to bear the same stress σ_1, and, as long as this is smaller than t_{s_0} (the tenacity of the weakest elements), no break will occur.

If the load is increased to p_2, obviously all fibers having a tenacity below t_{s_2} will break, and hence the actual tension in the sample will not be

$$\sigma_2 = \frac{p_2}{N_0 \cdot dq} = \frac{p_2}{dq \int_0^\infty \psi dt_s} \tag{23}$$

but

$$\sigma_2' = \frac{p_2}{N_2 \cdot dq} = \frac{p_2}{dq \int_{t_{s_2}}^{\infty} \psi dt_s} \tag{24}$$

Instead of the load p_2 being divided by the whole area under the curve of Figure 79, it must be divided by the area from t_{s_2} to infinity only. Hence the stress has been increased *automatically* by the ratio $\int_0^{\infty} \psi dt_s / \int_{t_{s_2}}^{\infty} \psi dt_s$.

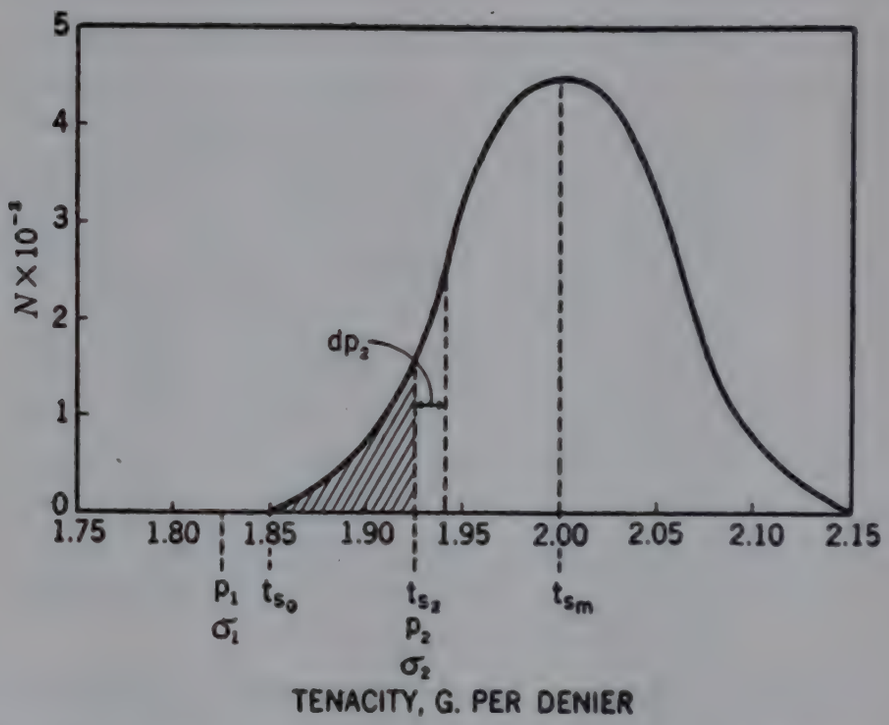

FIG. 79.—TENACITY DISTRIBUTION CURVE FOR A BUNDLE OF CELLULOSE FIBERS.

If another element of load dp_2 is now added, two increases of tension are obtained: (1) one which has been originated directly by adding dp_2; it amounts to

$$d\sigma_2 = \frac{dp_2}{N_2 \cdot dq} \tag{25}$$

(2) one which occurs automatically, due to the fact that all filaments having tenacities between t_{s_2} and $t_{s_2} + dt_{s_2}$ will now break and, hence, decrease the remaining cross section of the sample; this increase of tension is

$$(d\sigma_2)' = \sigma_2 \cdot \frac{\psi dt_{s_2}}{\int_0^{\infty} \psi dt_s} \tag{26}$$

The number of elements which break upon adding dp_2 is ψdt_{s_2}, and the number of the elements remaining unbroken is $\int_{t_{s_2}}^{\infty} \psi dt_s$. The ratio of the two indicates to what extent the remaining elements have to bear additional load.

As soon as the automatic stress $(d\sigma_2)'$ becomes greater than or even equal to the direct stress $d\sigma_2$, the whole system will break, because the filaments of each range of tenacity dt_s will put enough additional tension on the next ones to cause rupture, and this will go on until all individual filaments are broken.

Hence, the tension at which the bundle will break will be given by

$$d\sigma_2 = \sigma_2 \frac{\psi dt_{s_2}}{\int_{t_{s_2}}^{\infty} \psi dt_s} \tag{27}$$

or:

$$\sigma_2 = \text{breaking tension of the bundle} = \frac{\int_{t_{s_2}}^{\infty} \psi dt_s}{\psi}$$

$$= \frac{1 - \int_0^{t_{s_2}} \psi dt_s}{\psi} \tag{28}$$

If an analytical expression for ψ is known, equation (28) can be solved graphically and the bundle tenacity can be determined. Obviously, it will always be smaller than the mean or average tenacity of the single elements if broken individually. In Figure 79, t_{sm} represents this average tenacity, while $\sigma_2 = t_{s_2}$ determines the strength of the bundle.

Peirce and his collaborators[10, 37–39] have carried out measurements with cotton yarns, which show that both types of imperfections—the one along and the one across the sample—exist, and that both of them decrease the tenacities of such samples to a considerable degree. They report, for example, that 100 bundles of 50 cotton hairs each were made, and the mean bundle breaking load was found to be 105 g. per bundle with a standard deviation of 15%. This represented only 39% of the mean individual fiber tenacity as obtained from single filament breaking tests. Furthermore, they found that, for two cottons (*Sakel* hairs and *Zaria* hairs), the breaking length for 1-mm. specimens was 58 and 45 km., while it decreased to 51 and 37 km. for 2-mm., and to 36 and 24 km. for 10-mm. specimens, respectively.

No systematic observations on bundle strength have yet been published on artificial fibers, but it may be justifiable to assume that such statistical

studies will be of a considerable value for the gradual development of better single fibers and better yarns.

Finally, at the end of this section, it seems appropriate to add Table 5 containing a list of the main mechanical properties of natural and synthetic filaments, in order to show which range of tenacities and elongations can be covered by materials such as cellulose and its main derivatives.

TABLE 5

TENSILE STRENGTH AND ELONGATION TO BREAK OF VARIOUS FIBERS

Substance	Tensile strength, g. per denier	Elongation to break, %
Crude hemp, bone-dry	Up to 9.0	2– 4
Crude hemp, air-dry	Up to 8.0	3– 5
Crude ramie, bone-dry	Up to 8.0	2– 5
Crude ramie, air-dry	Up to 7.0	3– 6
Cotton	2.7–4.8	4–10
Highly stretched viscose rayon, bone-dry	Up to 7.0	3– 5
Highly stretched viscose rayon, air-dry	Up to 6.0	4– 7
Tire cord viscose rayon, air-dry	3.50–4.00	9–12
Normal textile viscose rayon, air-dry	1.80–2.10	14–18
Highly stretched acetate rayon, air-dry	Up to 6.5	3– 6
Normal acetate rayon, air-dry	1.6–1.8	22–28
Normal cuprammonium rayon	2.0–2.4	15–20
Silk	3.4–4.4	20–25
Casein fiber	0.5–0.8	30–50
Wool	1.0–1.6	20–25
Nylon	4.5–5.5	15–25
Vinyon	2.5–4.5	15–19

(*e*) *Mechanical Properties of Films*

After having treated quite fully the problems which arise in connection with the mechanical testing of fibers, it will be necessary to deal only briefly with films. To justify this, there is much less experimental material available in literature dealing with cellulose foils compared with the numerous articles concerning the mechanical properties of fibers.

It seems, however, that the same fundamental principles which have been described in connection with fiber properties earlier in this section are responsible for the mechanical properties of cellulose films. In particular, the amount and character of the prevailing orientation, and the

ratio between crystallized and amorphous material in the sample are important. X-ray studies which have been carried out with cellulose films[44–47] show that such films can exhibit a large number of different types of orientation which affect their mechanical behavior considerably.

As in the case of fibers, it is found that the tenacity increases in the direction parallel with the axial orientation and decreases in the perpendicular direction. On the other hand, the elongation to break parallel to the axis of orientation goes down to very low values (around 3%), while the elongation to break in the transverse direction assumes values up to 30% and more.

In the case of films, it may again be emphasized that there are a large number of empirical tests which aim mainly at the practical characterization of the samples without trying to connect this magnitude with any fundamental property of the material. On the other hand, there are a few tests carried out which approach more closely the design of a scientific experiment and furnish certain figures which may be related to the molecular and supermolecular structure of the samples.

In summary, it may be said that our present knowledge of the relationship between molecular and micellar structure of cellulose fibers and films and their mechanical properties is ample and extended only from a qualitative point of view. However, there are only very few data available on which to base a quantitative numerical relationship. There is no doubt that much interesting progress in this field could be achieved by increasing and improving the available quantitative experimental results.

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[44] E. Burgeni, O. Kratky, and K. Weissenberg, *Z. physik. Chem.*, **B4**, 401 (1929).
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[46] W. A. Sisson, *J. Phys. Chem.*, **40**, 343 (1936); **44**, 513 (1939).
[47] W. A. Sisson and G. L. Clark, *Ind. Eng. Chem., Anal. Ed.*, **5**, 296 (1933).

3. Strength of Native Fibers and Yarns

R. F. Nickerson

Cellulose is abundantly and widely distributed in nature where, together with other substances such as lignin, pentosans, and pectins, it forms the skeletal material of plant tissues. By reason of this function, cellulosic substances frequently occur as fibers which can be separated more or less readily from the surrounding matter.

The fibrous or filamentary character of the more common cellulosic

materials undoubtedly plays a role in the preparation and behavior both of pulps to be used for the manufacture of derivatives and of pulps for paper and allied substances. It attains its greatest importance, however, where the unmodified fibers are converted directly to textiles and cordage. In these uses, strength, length, and durability of fibers are pre-eminent and, in conjunction with such factors as fineness, color characteristics, and economy, largely determine the applications of the fiber and the quantities utilized.

(*a*) *Classification of Fibers*

Although there is an almost unlimited number of different native fibers, actually, the commercially important ones constitute a very small group because of the factors mentioned above. Classified by origin in the plant, this group separates into four subdivisions as follows (see also Chapter VI):

Seed Hairs: Fibers occur on or around the fruit. In the case of cotton, the most prominent member of the class, each fiber is part of a single cell.

Bast Fibers: Fibers occur in the bast or phloem of plants, that is, just beneath the bark or cuticular layer of the stem. Unlike cotton, single bast fibers, such as flax and jute, represent many small bast cells of elongated character.

Structural Leaf Fibers: Fibers occur in long, sword-like leaves. Like bast fibers, this type is multi-celled and is exemplified by sisal and Manila hemp.

Whole Stems: Fibers are small and occur throughout plant stems, such as tree wood and straw, more or less completely consolidated with noncellulosic substances.

Estimates, compiled from several sources,[1, 2, 3, 4] of fiber and cell dimensions for some of the more familiar materials are given in Table 1. It should be understood that the extent of cultivation throughout the world and the appreciable differences between varieties preclude the assignment of narrow limits to these dimensions. In addition to the fibers mentioned, many others have been suggested or used,[3] but, except in the case of unusual world conditions, their importance is not likely to increase in the face of the rapidly developing synthetic fiber industry.

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[1] C. Beadle and H. P. Stevens, *J. Soc. Dyers Colourists*, **30**, 94 (1914).

[2] J. T. Marsh and F. C. Wood, *Introduction to Chemistry of Cellulose.* Chapman & Hall, London, 1938.

[3] J. M. Matthews, *Textile Fibers.* 4th ed., John Wiley, New York, 1924.

[4] E. Sutermeister, *Chemistry of Pulp and Paper Making.* 3rd ed., John Wiley, New York, 1941.

The data indicate that cotton is one of the finest and most uniform of the unmodified native fibers. These two characteristics are of especial significance in the production of fine yarns and textiles. At the other extreme are

TABLE 1

APPROXIMATE SIZES OF MAJOR FIBERS AND CELLS[1-4]

Fiber	Type of fiber	Fiber length, cm.	Fiber width, mm.	Cell length, mm.	Cell width, μ
Cotton	Seed Hair	1.5–5.6	0.012–0.025	15–56	12–25
Flax	Bast	20–140	0.04–0.62	4–66	12–76
Jute	Bast	150–360	0.03–0.14	0.8–5	10–25
Hemp	Bast	100–300	.....	5–55	16–50
Ramie	Bast	10–180	0.06–9.04	60–250	16–126
Manila hemp	Leaf	180–360	0.01–0.28	3–12	12–46
Sisal hemp	Leaf	75–120	0.10–0.46	1.5–4	16–32
Wood	Stem	...	.....	0.14–5	Variable

the coarse, stiff, nonuniform fibers like sisal, which are more suitable for cordage and bristles. Intermediate types, such as jute, find application in coarse sack fabrics.

(*b*) *Fiber Strengths*

Approximate tensile strengths of the major fibers and derived products, compiled from various sources,[1, 3, 5–18] are summarized in Tables 2 and 3. These values also exhibit wide variation not only from environmental and

[5] S. G. Barker, *J. Textile Inst.*, **30**, P273 (1939).

[6] G. L. Carter and P. M. Horton, *Ramie.* Louisiana State Univ. Studies No. **26**, L. S. U. Press, Baton Rouge, 1936.

[7] C. M. Conrad and E. E. Berkley, *Textile Research*, **8**, 341 (1938).

[8] W. J. Cowden, *J. Textile Inst.*, **18**, P58 (1927).

[9] H. Jefferson, *Textile Colorist*, **49**, 254, 599, 677, 747 (1927).

[10] R. O. Herzog, *Ges. Abhandlungen des Kaiser-Wilhelm Instituts für Faserstoffchemie*, 1920–1922.

[11] R. Houwink, *Elasticity, Plasticity and Structure of Matter.* University Press, Cambridge, 1937.

[12] S. Kjellstrand, *Monatschr. Textil-Ind.*, **50**, 254, 278 (1935).

[13] H. Mark, *Physik und Chemie der Cellulose.* J. Springer, Berlin, 1932.

[14] H. Mark, *Trans. Faraday Soc.*, **29**, 6 (1933).

[15] H. B. Richardson, T. L. W. Bailey, and C. M. Conrad, U. S. Dept. Agr., *Tech. Bull.* **545** (1937).

[16] A. J. Stamm, U. S. Dept. Agr., *Misc. Pub.* **240** (1936).

[17] H. Mark, *Melliand Textilber.*, **10**, 695 (1929).

[18] K. C. Brown, J. C. Mann, and F. T. Peirce, *J. Textile Inst.*, **21**, T186 (1930).

varietal factors but also probably from the experimental techniques which have been employed in measurement. A systematic investigation of fiber strengths would furnish many data needed to supplement present knowledge.

TABLE 2

APPROXIMATE STRENGTHS OF MAJOR VEGETABLE FIBERS

Fiber	Range, kg. per mm.^{2}	Average, kg. per mm.^{2}	Elongation, %	Mean breaking length,[a] km.
Cotton	35–80[7, 15]	55[7, 15]	6–8	30[18]
Flax	40–110[11, 14]	80	1.6[5]	52[5]
Jute	40–80	60	0.8[5]	33[5]
Hemp	80–92[14]	85	1.6[5]	55[5]
Ramie	70–80[14]	75	2.7[5]	50
Wood (grain direction)	7–15[17]	11	..	5

[a] Length required to break under its own weight.

NOTE: Superscripts indicate sources; values not identified by superscripts are estimates selected from available data.[1, 3, 5–18]

TABLE 3

ESTIMATED YARN STRENGTH CHARACTERISTICS OF VEGETABLE FIBERS[1, 3, 5–18]

Fiber	Tensile strength, kg. per mm.^{2}	Mean breaking length,[a] km.
Cotton	10–25	12
Flax	30–50	24
Jute	15–25	11.5
Hemp	30–50	20
Ramie	20–40	20
Manila hemp	20–40	20
Sisal	20–40	20
Paper	0.5–8.0	2
German paper yarn	..	6

[a] Length required to break under its own weight.

Inspection of Tables 1 and 2 suggests that fiber strengths may vary somewhat with the lengths of the constituent fiber cells, and hence that the overlapping and bonding of cells is a factor in strength development. Again, however, more convincing data are required.

The upper limit of strength given for flax fibers is unusual and represents a careful laboratory treatment to effect a further orientation of the highly oriented natural product. Mark[17] (see Section G, 1 of this chapter) has calculated a theoretical rupture strength of 800 kg. per mm.^{2} for primary

valence bonds in cellulose. The discrepancy between theoretical and observed strengths may result from (a) imperfections in the macro structure; (b) nonorientation of the crystallites in respect to the direction of stress; (c) inequalities in length of fiber elements and a consequent uneven distribution of load at the point of rupture; and (d) testing methods which measure only the minimum strength of specimens. The effects of imperfections are probably appreciable, since Brown, Mann, and Peirce[18] have shown from repeated breaking of the same cotton fibers that the loads required for the second and third breaks are often double or treble the initial ones. Conrad and Berkley,[7] Berkley,[19] Sisson,[20] and Morey[21] have found that cotton and other fibers are stronger, the more nearly parallel the long axes of crystallites are to the long axes of the fibers. Elongation appears to vary inversely. Inequalities in cotton fibril lengths have also been suggested[18] as an explanation of some strength phenomena.

The data on paper and paper yarns are included in Table 3 as being indicative of the order of magnitude of van der Waals' or secondary valence forces, which appear to account for much of the bonding of fibers in unsized paper. Mark[17] (see Section G, 1 of this chapter) derived for this case a theoretical value of 200 kg. per mm.^{2}, corresponding to a breaking length of about 47 km. Breaking length, that is, the length which would break under its own weight, is frequently used in paper testing and in other cases where cross-sectional area is not known. Again, it is evident that actual values fall far short of the calculated maxima.

Cotton, unquestionably the most important economically of the native fibers, has been most carefully and completely investigated. As single cells of high natural purity, the individual fibers have a broad field of application and, in addition, have frequently served as source material in theoretical studies. Many of the available mechanical, physical, and analytical data on single cotton fibers have been summarized in the literature.[22] In the absence of similar extensive data on the other fibers, the following discussion draws heavily on cotton researches, but it is possible that, to some extent, the information given typifies the behavior of single cells of the other fibers.

A tensile strength of 55 kg. per mm.^{2} for cotton, corresponding to about 80,000 lbs. per sq. in., appears to be better substantiated than the widely quoted value of 28 kg. per mm.^{2}. Chandler bundle strengths yield estimates

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[19] E. E. Berkley, *Textile Research*, **9**, 355 (1939).
[20] W. A. Sisson, *Textile Research*, **7**, 425 (1937).
[21] D. R. Morey, *Textile Research*, **4**, 491 (1934).
[22] R. F. Nickerson, *Ind. Eng. Chem.*, **32**, 1454 (1940); **34**, 1149 (1942).

ranging from 60,000 lbs. per sq. in. for coarse cottons to 120,000 lbs. per sq. in. for the very fine.[7, 15, 19]

(c) *Yarn Strengths*

Approximately half the potential strength of natural fibers is sacrificed when fibers are converted to yarns and cordage.[5] This fact is shown by the data in Tables 2 and 3. All practicable yarns are made by twisting, and, obviously, the shorter the constituent yarn fibers are, the more necessary higher twists become. However, almost any torsion at all appears to weaken single fibers appreciably.[7] This effect tends to a maximum in the coarse, highly oriented fibers like ramie.[23] Thus, yarn strength is a compromise between the weakening effects of twist and the strengthening influence of fiber cohesion. Campbell[24] has pointed out that the amount of twist corresponding to maximum cotton yarn strength varies with fiber length.

Cotton, the most carefully studied fiber, serves as an illustration. As the fibers are relatively short, many of them must end in a cross section of yarn or so near it that, at rupture, they slip rather than break. Fiber shortness requires that high twist ratios be employed to develop maximum fiber-to-fiber clinging, but twisting apparently produces shearing strains which contribute to rupture,[7] although over-twisting frequently has advantages.[25] It has been reported[26, 27, 28] that there is no correlation between cotton fiber strengths and yarn strengths. About 70% of the fibers in a cross section of well-made yarn may break at rupture,[26] but seldom is more than half the potential strength of cotton fibers realized. Conversely, the longer fibers require lower twists, and a higher percentage of those traversing a cross section participate in bearing the load. In general, the longer and finer fibers, such as Sea Island cotton, flax, and Manila hemp, make the stronger yarns.

(d) *Factors Which Modify Fiber and Yarn Strengths*

Moisture. Some form of retting is usually employed in the isolation of bast and leaf fibers. Indirectly, this indicates that continuous exposure

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[23] L. H. Dewey, U. S. Dept. Agr., *Misc. Circ.* 110 (May, 1929).
[24] M. E. Campbell, *Textile Research*, 8, 263 (1938).
[25] S. A. Steere, U. S. Patent 1,632,201 (June 14, 1927).
[26] G. G. Clegg, *Shirley Inst. Mem.*, 5, 223 (1926).
[27] A. J. Turner, *J. Textile Inst.*, 19, T286 (1928).
[28] N. W. Barritt, *J. Textile Inst.*, 20, T70 (1929).

to wet conditions produces, at most, only a slow fiber degradation. This water resistance of the hard fibers is valuable in marine cordage, such as ships' ropes and fish nets. A large part of the strength loss of fibers in water is probably the result of mildewing,[29] that is, attack by microorganisms.

The strengths of native fibers and of yarns or cords made from them vary directly with moisture content, which, in turn, is more or less completely dependent upon temperature and relative humidity (R.H.). In general, increase in moisture content promotes appreciable increases in yarn or cord strengths[3] while dehydration has the opposite effect. This behavior is especially important in paper and textile testing.

Cotton fiber breaking-strengths increase with rising relative humidity and come to a maximum at, and remain constant above, 60–70% R.H.[18, 30] Brown, Mann, and Peirce[18] found average cotton fiber strengths of 3.5 g. at 15% R.H. and 5.2 g. at 100% R.H. for the same cotton. Wet fiber strengths are said to be 110 to 120% of the air-dry strengths.[31]

Cotton fibers become less rigid,[32] more plastic,[33] and more extensible[18] as they acquire moisture. Extensibility increases proportionally faster than does breaking load with rising humidity and varies from 5.3% at 10% R.H. to 9.5% at 100% R.H. That the extension of moist fibers is partly a result of fibril straightening is suggested by the improved orientation pattern obtained from fibers wetted, stretched, and dried in the stretched condition. Such lability of the fibrils may permit the stress to distribute itself more uniformly over the cross section of the fiber with beneficial effects on strength.[18] The greater strength of highly oriented fibers has already been mentioned.

The variation of cotton yarn strength with humidity[34] is shown in Table 4. These data also indicate the type of relation that exists. The same investigations show that, for other cotton yarns, the strength at 100% R.H. is 135 to 160% of the bone-dry strength. Part of this increase is attributed to increased fiber strengths and part to other factors.[18, 30] If fiber strengths are not correlated with yarn strengths, as has been suggested,[26, 27, 28] then the other factors are appreciable. Considerable yarn

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[29] M. S. Furry, H. M. Robinson, and H. Humfeld, *Ind. Eng. Chem.*, **33**, 538 (1941).

[30] J. C. Mann, *Shirley Inst. Mem.*, **6**, 53 (1927).

[31] J. Obermiller and M. Goertz, *Melliand Textilber.*, **7**, 163 (1926).

[32] F. T. Peirce, *Shirley Inst. Mem.*, **3**, 253 (1924).

[33] F. T. Peirce, *Shirley Inst. Mem.*, **2**, 278 (1923).

[34] F. T. Peirce and R. J. Stephenson, *Shirley Inst. Mem.*, **5**, 239 (1926).

strength is gained between 70 and 100% R.H., a region in which fiber strengths are practically invariant.

The yarn strength-moisture relation of cotton appears to be influenced considerably by the variation of fiber rigidity, plasticity, and extensibility with humidity. With increasing fiber moisture content, these properties are changing so as to promote better fiber-to-fiber clinging. After dehydration, however, the augmented rigid properties tend to oppose yarn collapse and thus hinder the maximum development of mutual fiber contacts. The lower elongation of dry fibers acts to produce greater inequalities in stress distribution at rupture. Aging and dehydration of the coarser fibers such as jute and ramie cause them to become brittle and to fracture easily.[3]

TABLE 4

EFFECT OF HUMIDITY ON COTTON YARN STRENGTH (PEIRCE[34])

Relative humidity (%)	Dry[a]	30	50	70	85	92	100
Breaking load (g.)	160	186	195	207	214	217	218
Extension at break (mm.)	22	23	29	31	35	35	35

[a] Extrapolated.

Heat. The effects of heat on the strength of native fibers are related through dehydration to the moisture phenomena just described. If relative humidity is held constant, high temperatures decrease the rigidity of cotton fibers[32] and increase the plasticity.[33, 35] Stoll[36] has observed a 15% loss in strength of cotton tire cord heated for 2 hrs. at 140–150°C., but, on the basis of the experiments of Houtz and McLean,[37] this finding may be the result of a temporarily decreased moisture regain capacity. At temperatures above 150°C., cellulose is probably damaged permanently.

The wetting, stretching, and drying of cotton yarns increase strength but introduce strains which persist as long as the fibers are dry and the fiber elements immobile. Moist heat causes a rapid relaxation of the distorted inner fiber structure where there is no stress on the fibers. Under suitable high-temperature conditions, however, relaxation with loss in yarn strength may occur even though the yarn carries a full load.[38] The heat, moisture,

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[35] G. E. Collins, *Shirley Inst. Mem.*, **2**, 204 (1923).

[36] L. Stoll, *Gummi-Ztg.*, **43**, 2218 (1929).

[37] C. C. Houtz and D. A. McLean, *J. Phys. Chem.*, **45**, 111 (1941).

[38] R. F. Nickerson, U. S. Patent App. Ser. No. 342,697 (June 27, 1940).

rigidity, and lability phenomena are encompassed in domestic ironing operations.

Acids. Acids lower fiber strengths at speeds subject largely to temperature, and type and concentration of acid. At intermediate and higher temperatures, the mineral acids are especially detrimental. For example, cotton is completely tenderized by hot 1 *N* hydrochloric acid in one minute.[39] Organic acids act more slowly. At sufficiently low temperatures, even the strong acids are not destructive over short periods of time. For example, it is claimed[40] that the nitration of cellulose can be conducted without appreciable degradation if the temperature is low and water is continually removed. The cleavage of primary valence bonds in expanded, amorphous, intercrystalline fiber regions may be responsible for the tendering. The product of acid attack is hydrocellulose.

TABLE 5

BREAKING LENGTH OF SINGLE COTTON FIBERS (BROWN, MANN, AND PEIRCE[18])

Fiber	Breaking length, km.
Texas, raw	27
Texas, soda-boiled	27
Texas, mercerized	25
Sakellarides	37–38

Alkali. Dilute alkali in the absence of oxygen exerts but little influence on fiber strengths. The data of Brown, Mann, and Peirce[18] in Table 5 reveal that soda-boiled cotton fibers are similar in strength to raw fibers. Soda- or kier-boiling removes waxes and pectates from fibers. This operation generally increases the strength of a yarn, probably by extraction of the natural wax which acts as a fiber lubricant.[3] Vincent[41] has found that a short treatment of cotton yarn with dilute sulfuric acid before the soda-boiling increases the final strength.

Cold, concentrated sodium, potassium, cuprammonium, and quaternary ammonium hydroxides, under suitable conditions, mercerize native fibers. As the data in Table 5 show, individual fiber strengths are not much changed by mercerization, but yarns may gain as much as 50% of their original strengths as a result of the treatment. It is possible that mercerization lowers fiber rigidity by increasing the amount of noncrystalline,

[39] H. F. Coward, F. C. Wood, and F. L. Barrett, *J. Textile Inst.*, **14**, T520 (1923).

[40] E. Berl, *Ind. Eng. Chem., Anal. Ed.*, **13**, 322 (1941).

[41] P. D. Vincent, *J. Textile Inst.*, **15**, T281 (1924).

nonrigid cellulose,[42, 43, 44] and thus facilitates production of dense, flexible yarns.

In the presence of oxygen, alkali promotes the formation of oxycellulose and causes a proportionate loss in fiber strength. Standard viscosity measurements[45, 46] are commonly used to determine the extent of hydrolytic and oxidative degradation of cotton fibers and yarns. The reduction in viscosity or increase in fluidity is closely correlated with loss in strength.[47]

Salts. The action of salts on fibers is variable and depends chiefly upon the conditions and the character of the salt. Acidic salts may cause hydrolytic degradation, while alkaline salts, in the presence of heat or light, may produce oxidative destruction. High concentrations of certain salts, notably $ZnCl_2$, $Ca(CNS)_2$, and LiCNS, appear to cause intermicellar swelling and mercerization.[48]

Light. Intense light rapidly lowers the strengths of both cotton fibers and cotton yarns,[49] but it is claimed[50] that ultraviolet radiation, in quantities insufficient to form detectable amounts of oxycellulose, increases the strength of cotton goods. Exposure of cotton to ozonized air at 75 to 150°C. also is said to improve strength.[51]

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[42] R. F. Nickerson, *Ind. Eng. Chem.*, **34**, 85 (1942).
[43] W. A. Sisson and W. R. Saner, *J. Phys. Chem.*, **45**, 717 (1941).
[44] H. Mark, *J. Phys. Chem.*, **44**, 764 (1940).
[45] D. A. Clibbens and A. Geake, *Shirley Inst. Mem.*, **6**, 117 (1927).
[46] E. K. Carver and Committee, *Ind. Eng. Chem., Anal. Ed.*, **1**, 49 (1929).
[47] D. A. Clibbens and B. P. Ridge, *Shirley Inst. Mem.*, **7**, 85 (1928).
[48] J. R. Katz and J. C. Derksen, *Rec. trav. chim.*, **50**, 149 (1931).
[49] P. W. Cunliffe and F. D. Farrow, *Shirley Inst. Mem.*, **7**, 1 (1928).
[50] P. B. Cochran, U. S. Patent 1,699,779 (Jan. 22, 1929).
[51] A. J. Pacini, U. S. Patent 1,948,276 (Feb. 20, 1934).

Chapter X

TECHNICAL APPLICATIONS OF THE PHYSICAL PROPERTIES OF CELLULOSE AND ITS DERIVATIVES

X. TECHNICAL APPLICATIONS OF THE PHYSICAL PROPERTIES OF CELLULOSE AND ITS DERIVATIVES

W. E. Gloor

The definition of the word "technical" appearing first in the second edition of Webster's New International Dictionary reads: "Of or pertaining to the useful or mechanic arts, or any science, business, profession, sport, or the like; specially appropriate to any art, science, business, or the like." Certain it is that this definition is no broader than the applications of cellulose, the toughness of which is used to advantage in such delicate procedures as preparing collodion mounts for specimens under the electron microscope; in such bludgeoning tasks as being driven into the earth to serve as piling; or, to strike a sporting note, in giving the batsman a dependable tool with which to hit the ball, be the game baseball, cricket, or jai alai. To cover such a wide field demands a selective approach, in which it is proposed to discuss the forms of cellulose now used industrially in the terms of physical-chemical properties and economic relations which fit them to these purposes.

The great economic importance of these industrial uses may be illustrated by the fact that, of the twenty groups of industries set up by the U. S. Department of Commerce in its Census of Manufactures (1939), six groups are largely concerned with the handling of cellulose in one form or another: textiles, apparel from fabrics, lumber, furniture and lumber products, paper and allied products, and printing and publishing. These industries comprise about 40% of the business establishments, employ 39% of the wage earners and 33% of the salaried workers in industry, and their products are valued at 25% of the national total. Add to this the not inconsiderable role played by cellulose and its products in the chemical, rubber, electrical, and automobile manufacturing groups, and it is apparent that the material is of vital importance as a raw material to an industrial nation and as a salable product to an agrarian economy.

A. NATURAL CELLULOSE

The vegetable fibers of commerce embrace the cellulose which finds commercial use much as it occurs in nature. The kinds and sources of cellulose have been given in Chapter I, but a summary of the uses of the various kinds will be given here in Table 1.

TABLE 1

USES OF NATIVE CELLULOSES (DEWEY[1] AND MATTHEWS[2])

A. Spinning Fibers
   1. Fabric fibers.
      (a) First-rank fibers, for spinning and weaving into fine and coarse textures (domestic uses, awnings, sails, etc.; fibers include cotton, flax, ramie, hemp, and pineapple).
      (b) Second-rank fibers, for coarse uses (burlap, gunny, cotton bagging, mats, floor coverings, etc.; fibers include coir and jute).
   2. Netting fibers.
      (a) Lace fibers, which are cotton, flax, ramie, agave, etc.
      (b) Coarse netting fibers, for all forms of nets, and hammocks. Cotton, flax, ramie, and New Zealand flax are used commercially.
   3. Cordage fibers.
      (a) Fine spun threads and yarns other than for weaving; cords, lines, and twines. All the commercial fabric fibers are used, also sunn, sisal, coir, Manila, pandanus fiber, seaweed (for fishlines), and New Zealand flax.
      (b) Ropes and cables, chiefly hemp, and sisal and Manila hemps in commerce.

B. Tie Material (*rough twisted*)

   Coarse growths, such as stripped palm leaves or peeled bark of trees, used without preparation.

C. Natural Textures
   1. Tree basts, with tough, interlacing fibers.
      (a) Substitutes for cloth, prepared by simple stripping and pounding; the tapa or kapa cloth of the South Sea Islands.
      (b) Lacebarks, used for cravats, frills, whips, thongs; *Lagetta lintearia* found in Jamaica.
   2. Ribbon or layer basts, such as Cuba bast, once used to tie up bundles of Havana cigars and for making cordage and bags.
   3. Interlacing structural or fiber sheaths.

D. Brush Fibers
   1. Brushes manufactured from prepared fiber.
      (a) For soft brushes; animal-hair substitutes, as Tampico fiber.
      (b) For hard brushes; palmetto, palmyra, and kittul fibers.

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[1] L. H. Dewey, *Year Book of the U. S. Dept. Agr.* Washington, 1903, p. 387.

[2] J. M. Matthews, *The Textile Fibers.* 4th ed., John Wiley, New York, 1924, p. 328.

2. Brooms and whisks.
   (a) Grass-like fibers; broomroot and broomcorn.
   (b) Bass fibers; Monkey bass.

E. Plaiting and Rough-Weaving Fibers

1. Hats and sandals.
   (a) Straw plaits from wheat, rye, barley, and straw; *e. g.*, Tuscan and Japanese braids.
   (b) Plaits from split leaves, chiefly palms; *e. g.*, Panama hats from *Carludovica palmata*.
   (c) Plaits of bast and thin woods used in millinery.
2. Mats and mattings; also thatch materials.
   (a) Commercial mattings from rush: sleeping mats, screens.
   (b) Thatch roofs from tree basts, palm leaves, grasses.
3. Basketry.
   (a) From woody fiber.
   (b) From whole or split leaves or stems.
4. Miscellaneous: willowware, rush chair bottoms, etc.

F. Various Forms of Filling

1. Stuffing or upholstery.
   (a) Wadding, batting, etc., commercial cotton lint.
   (b) Cushion-filler: cotton, seed hairs, kapok, etc.
   (c) Mattress and furniture filling: tow or waste of prepared fiber, unprepared bast, straw and grasses, Spanish moss, etc.
2. Caulking.
   (a) Filling seams in vessels: oakum from fibers, coir fiber.
   (b) Filling seams in casks: giant grasses.
3. Substitute for hair in plaster, New Zealand flax, palmetto fiber.
4. Packing.
   (a) In bulkheads, etc.; cellulose from corn pith, coir.
   (b) In packing glands of pumps, engines, etc.; linen and soft fibers.
   (c) For protection in transportation; various fibers, soft grasses, excelsior.

G. Paper Material

1. Textile papers.
   (a) The spinning fibers in the raw state, mill waste, tow, jute-butts, Manila rope, etc.
   (b) Spun cotton or flax, in the form of rags.
2. Bast papers: for example, the paper mulberry.
3. Palm papers: palmetto and yucca papers.
4. Bamboo and grass papers, such as esparto.
5. Wood pulp cellulose.
   (a) Mechanical pulps; ground wood.
   (b) Chemical pulps; sulfite, soda, and sulfate pulps.

H. Chemical Cellulose

1. Purified cotton linters.
2. "Dissolving pulps," generally sulfite wood pulp.

Matthews[3] states that perhaps 700 different vegetable fibers are in use by the human race, but most of the exotic fibers are unimportant or are employed only in the localities where they grow. The important vegetable fibers are used chiefly in textiles. Matthews lists the technical properties required in a textile fiber as: high tensile strength, which is most important, since it affects resistance to wear; length of fibers, since thread strength is proportional to the length of the fiber used in spinning it; cohesiveness, which gives high surface friction between adjacent fibers in a thread (the twists and kinks in cotton fiber and the knots in linen fiber promote this); pliability, which enables a fiber to spin without breaking; fineness of staple, "the finer the staple the finer the yarn," the coarse fibers such as jute, sisal, and hemp giving crude fabrics like bagging, burlap, and cordage; uniformity of staple, regularity in length and diameter of the fiber giving more even thread; porosity, or ability to absorb liquid, permitting dyeing and bleaching; luster, affecting beauty, sales appeal but hardly usefulness; resistance to wear. The economic factors which make a vegetable fiber attractive to commerce are a constant supply of a large quantity of the fiber and the ready marketability at a cheap price. The commercially important fibers to be discussed in the next sections are cotton, linen, jute, hemp, and sisal.

It has been shown in Chapter I, p. 9, that the various textile fibers in commercial use are found to be aggregations of 2000 or more anhydroglucose units, as they occur in nature. To the technologist, the important thing is that these fibers as he gets them are eucolloids[4] composed essentially of the long-chain polymer, cellulose. Further, as Neale[5] emphasizes, technical interest attaches not so much to the original molecular weight of the natural cellulose, but is chiefly directed to finding a practical answer to the question of how little the cellulose can be depolymerized, in the process of purification and coloring, so as to preserve its tenacity to the greatest extent.

1. Cotton

The wide textile use made of cotton in all localities in which it has been available, dating from 3000 B.C. in India,[5a] doubtless arose because its seed hairs are the purest forms of natural cellulose which combine the requisite properties. The long fibers, $^{7}/_{8}$ in. or more, and their twisted, kinked struc-

[3] J. M. Matthews, *The Textile Fibers*, p. 7; see ref. 2, p. 1056.
[4] H. Staudinger, *Naturwissenschaften*, **42**, 673 (1937).
[5] S. M. Neale, *Chemistry & Industry*, **1936**, 602.
[5a] A. N. Gulati and A. J. Turner, *J. Textile Inst.*, **20T**, 1 (1929).

ture were found to lend themselves most readily to spinning into strong yet thin threads. The superior fineness of some of the Indian muslins to anything of Western manufacture, with a texture which has led to their description as "webs of woven wind," is ascribed by Matthews not to the use of any superior varieties of cotton fiber, but to the skilfulness and patience of the workmen in using the distaff, and the very small production of such fabrics.

TABLE 2

PRODUCTION OF COMMERCIAL COTTON IN THE WORLD (MERRILL, MACORMAC, AND MAUERSBERGER[6])

Figures in Thousands of Bales

Season	U. S.[a]	India[b]	Russia[b]	China[b]	Brazil[b]	Egypt[b]	Minor producers	World total	N. Y. spot prices[c] (cents)
1910–11	12,202	3202	1026	795	287	1515	843	19,870	15
1914–15	16,231	4153	1304	785	395	1298	883	25,049	8
1920–21	13,664	3250	58	1235	406	1198	817	20,628	15
1926–27	18,162	4002	830	1378	442	1649	1467	27,930	13
1930–31	13,873	4590	1589	1715	401	1698	1510	25,376	11
1936–37	12,375	5661	3400	3020	1751	1863	2659	30,729	12
1939–40	11,817	4420	4000	627	2094	1785	2925	27,367	10
1940–41	12,566	...	...	...	...	...	...	...	..
1941–42	10,744	...	...	...	...	...	...	...	..
1942–43	12,982[d]	...	...	...	...	...	...	...	..

[a] Figures in running bales of 500 lbs.

[b] Foreign figures in statistical bales of 478 lbs.

[c] Spot prices are averaged from the chart appearing on p. 54 of the reference from which this table was taken.

[d] Estimate, based on figures in U. S. Dept. Agr., *Cotton Report*, Dec. 1, 1942.

While the primacy of cotton in textiles has been threatened of late by the rise of synthetic yarns based chiefly on cellulose from wood, even in countries where such changes have not been instigated by policies of national self-sufficiency, today cotton is by far the most widely used textile fiber. Production and consumption of cotton in textiles is illustrated by Tables 2 and 3.

The applications of the knowledge of the molecular structure of cellulose to the manufacture of cotton textiles appear to be numerous and of recent elucidation. Knowledge of the coarser structures, such as has been reviewed for a number of textile fibers recently by Alexander,[7] is of some

[6] G. R. Merrill, A. R. Macormac, and H. R. Mauersberger, *American Cotton Handbook*. Am. Cotton Handbook Publishing Co., New York, 1941, p. 42.

[7] J. Alexander, *Ind. Eng. Chem.*, **31**, 630 (1939).

value in explaining behavior of dyestuffs. It has been shown by several workers[9, 10, 11] that the dye absorption of substantive dyes by cellulose, notably cotton cloth, is largely influenced by the particle size of the dye micelle. It is reported[11] that dyeings from solutions containing dye particles of radius larger than 2×10^{-7} cm. are from one-tenth to five-tenths the strength of those prepared from solutions containing particles with radii smaller than 1.7×10^{-7} cm., and that these dimensions are of the order of those estimated for the size of the submicroscopic pores in

TABLE 3

CONSUMPTION OF COTTON IN THE UNITED STATES (MERRILL, MACORMAC, AND MAUERSBERGER[8])

Season	Active spindles	Bales of cotton consumed
1941–42	...	11,172,328
1940–41	23,389,000	9,721,703
1939–40	23,585,938	7,783,774
1936–37	25,419,440	7,950,079
1930–31	28,979,646	5,262,974
1926–27	34,409,910	7,189,585
1920	35,480,958	6,419,734
1915	31,964,235	5,597,362
1910	28,266,864	4,621,742

cotton.[12, 13] The use of many of the proprietary colloidal dye assistants as dyeing aids, first in wetting the fiber and then in equalizing shades and giving uniform penetration, is probably associated with the adsorption of these wetting agents on the surfaces of these pores, or with an increase in their state of aggregation in the dye bath.[14] The application of the multitude of finishing agents to improve the hand, feel, and drape of fabrics probably also is governed by adhesion to pore and fibril surfaces, although the ultimate effect as felt or seen by the consumer also involves the fiber, yarn, and weaving texture.[7]

While the textile use of cotton is still its major outlet, the cotton linters

[8] G. R. Merrill, A. R. Macormac, and H. R. Mauersberger, *American Cotton Handbook*, p. 68; see ref. 6, p. 1059.

[9] R. E. Rose, *Ind. Eng. Chem.*, **25**, 1265 (1933).

[10] W. Schramek and E. Götte, *Kolloid-Beihefte*, **34**, 218 (1932).

[11] S. Lenher and J. E. Smith, *Ind. Eng. Chem.*, **27**, 20 (1935).

[12] A. R. Urquhart and A. M. Williams, *Mem. Shirley Inst.*, **3**, 197 (1924).

[13] A. Frey-Wyssling, *Kolloid-Z.*, **85**, 148 (1938).

[14] A. Chwala *Textilhilfsmittel*. J. Springer, Vienna, 1939, pp. 354–5.

recovered by the oil mills in the United States are largely consumed in making chemical cotton. The process, outlined by Munson,[15] provides raw material for the acetate, cuprammonium, and sometimes the viscose rayon processes, for nitration into soluble or smokeless-powder types of nitrocellulose, for etherification of cellulose, for certain white floc fillers for plastics, etc. Of recent years the supply of linters from the oil mills has been augmented by use of hull fiber, with complete success in certain applications.

Efforts to widen the fields of application of cotton in recent years have included: use of resin-impregnated goods in propellers for aircraft[16]; use of cotton duck in road building, the canvas being laid over a bituminous surface and being covered with a tar or asphalt surface; surfacing of river levees with cotton sheeting given water-repelling treatments; use of heavy cotton weaves as a base for veneering; use of cotton duck side-wall covering for buildings, painted and applied like tarlatan in art galleries; making stationery from cotton cloth.[17] The use of the whole cotton plant as a source of alpha-cellulose has been extensively investigated; and it appears that the low alpha-cellulose content (80%)[18] of this raw material precludes its being treated by the relatively simple cook and bleach cycles used in preparing chemical cellulose from linters, making it a rather expensive competitor of wood pulp as a raw material for pulp processing. The spinnable cotton fiber still commands a real premium over the shorter-fibered celluloses. All these proposed uses are efforts to apply the high tensile and favorable elastic and durability properties of cotton cellulose.[19]

2. Linen

As a textile fiber, linen suffers the disadvantages of requiring treatment to obtain spinnable fibers from the flax bast, and of exhausting the soil in which it grows, requiring heavy fertilization if grown continually. The flax plant is grown extensively in the United States and the Argentine for oil, but in these areas the stalks are usually burned, since the fiber is not of the best quality.[20] In northern Europe the chief aim of flax culture is fiber.

Linen has the longest record of use by man of the fibers, having a history

[15] W. D. Munson, *Ind. Eng. Chem.*, **22,** 466 (1930).

[16] Anon., *Ind. Eng. Chem.*, **23,** 49 (1931).

[17] H. J. Skinner, *Ind. Eng. Chem.*, **24,** 694 (1932).

[18] D. T. Milne and F. K. Cameron, *Ind. Eng. Chem.*, **31,** 1076 (1939).

[19] G. R. Merrill, A. R. Macormac, and H. R. Mauersberger, *American Cotton Handbook*, p. 88; see ref. 6, p. 1059.

[20] J. M. Matthews, *The Textile Fibers*, p. 741; see ref. 2, p. 1056.

dating back 4500 years in Egypt. It finds its present uses because of its strength, its superior heat transfer as compared with cotton fabric (the yarns themselves have nearly the same specific heats, 0.321 versus 0.319), the high luster and stiff finish obtained when fabric is ironed, and the high absorbency for water. Linen sailcloths have been known to more than double their tensile strength simply by absorbing water. Linen rags still give the best raw stock for papermaking.

3. Jute

A still coarser bast fiber than linen, jute finds large industrial usage. The fiber, obtained from the ripe stalks by retting, drying, and scutching (the latter often a hand process), is the principal ingredient of burlap, cotton bagging, carpet backing, and such materials. The fiber structure is unusual in that the cellulosic portions are separated at $^1/_8$-in. intervals by lignified areas. The poor resistance of this fiber to weather, alkali, and bleaching probably results from this structure. Of low strength, its softness and ready spinnability are said to be the chief reasons for its use, which in volume is second only to cotton among the vegetable fibers.[21] Here is a case where the coarser structure of the fiber reinforces the lower D.P. of the cellulose in determining strength.

4. Hemp

The bast fibers of *Cannabis sativa* comprise the true hemp of commerce. The long, rather stiff fibers, obtained by a retting procedure similar to that used with linen, are used chiefly in cordage and twine, because of their weathering resistance, and seldom in textiles, because of harshness and embrittlement on bleaching.

Manila hemp is obtained from *Musa textilis*, a variety of plantain known in the Philippines, its chief source, as *abaca*. The fibers are obtained from the leaf sheath by slicing, drying, and hand stripping the strands, which may reach a length of 12 ft. It is the best fiber for making marine cordage which must resist the action of salt water, and for all heavy ropes or hawsers which must have great strength and flexibility. Fine fibers can be woven into acceptable muslins. An effort was made at one time to utilize waste Manila fiber in producing tough paper for cement bags, etc. Alexander[7] believes that the high xylan content of the fiber may act as a cohesive colloid between cellulose chains, and cites x-ray data showing the

[21] J. M. Matthews, *The Textile Fibers*, p. 771; see ref. 2, p. 1056.

cellulose in this fiber to be identical in cell dimensions with that found elsewhere.

5. Sisal or Agave

This fiber, obtained from the leaves of several varieties of the plant, is used chiefly in binder twine and general cordage, except that used for marine and hoisting purposes. It will not withstand salt water, and it is not flexible enough to run well over pulleys. Recent commercial efforts to utilize the strength of this fiber as a filler in making low-density thermosetting plastic shapes for military uses have met considerable success.[22]

6. Ramie

The raw material for many excellent scientific studies on cellulose, ramie occupies a much less significant place among the textile fibers of commerce. Although the fibers are long, strong, and fine as silk, they must be isolated from the plant by hand labor. Matthews states that in China a native can produce about 8 lbs. of cleaned ramie per day.[23] The fiber also must be degummed before it can be spun, and in 1932 it was stated[17] that no satisfactory chemical process for doing this had been devised, although Matthews gives details of a fermentation process said to have been used in Germany prior to 1914. Skinner believes that since it shows the most perfect crystallinity of all natural cellulose, this accounts for its lack of elasticity and twisting properties,[17] and that these properties are inherent and not simply the fault of improper preparation of the fiber. Since the smoothness of the fiber certainly is not an aid to easy spinning, and the hand cleaning is expensive, the trade status of the material today is probably similar to that of cotton before Eli Whitney invented the gin.

7. Pulp and Paper

This aspect of the use of natural cellulose comes not from the isolation and combination of the fibers more or less as they exist in the plant, but through the application of the swelling of cellulose in water. The fibers need not be long, and the attention of the industry is directed first to an elimination of noncellulosic impurities from the pulp, then to the proper swelling, matting together, and drying of the sheet of fibers. The production of papers is first credited to the Egyptians, whose civilization must

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[22] A. W. Koon, *Modern Plastics*, **18**, 63 (Aug., 1941).

[23] J. M. Matthews, *The Textile Fibers*, pp. 780–5; see ref. 2, p. 1056.

have been modern at least in cellulose consciousness for they used both linen and ramie in addition to papyrus. Until 1800, papers were all based on linen and cotton rags, with crude beating and sheet formation. The era of mechanical invention produced the tools with which to make paper, resulting in actual shortage of rags as a result of the expanding demand.[24] The early rag papers age remarkably well; made with crude chemicals, they probably were never as highly degraded as are most modern rag stocks, and were made in locations selected for pure water available in ample quantity.

The shortage of rags with which to meet the demands of a civilization dependent on paper for the spreading of knowledge, expansion of business and records, in which the large daily newspaper became more and more important in the daily life of the people, led to many efforts to find cheaper, more abundant supplies of papermaking material. Between 1800 and 1838, straw, beach grass, corn husks, sea grass and seaweed, sorghum stalk, Spanish grass, reeds, rope, canvas, corn stalks, and cotton stalks were patented in the United States as raw materials for the preparation of paper pulp. Straw pulp was probably the first to be commercialized under the Magaw patents.[25] Involving the beating of bleached straw into pulp and subsequent sheeting on a cylinder, the product is said to have been strong and durable, and, though slightly yellow, to have sold for as high as two dollars per ream.[24]

The development and chemical processes involved in the preparation of pulps by the various chemical processes now used are described in Chapters VI and VII. While paper may be simply defined as a felt made from cellulose fibers, the technique is quite complicated. In this survey the complexities of papermaking must be passed over, for lack of space in which to give a reasonably adequate treatment. The extent of the subject may be gained by consulting modern works on the art.[26–30]

The point should be made, however, that paper has come into its own as an industrial material in the last thirty years. The large proportion of

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[24] Anon., *Paper Trade J.*, 111, Sect. II, 8 (Nov. 28, 1940).

[25] W. Magaw, U. S. Patents issued on Mar. 8 and May 22, 1828.

[26] E. Sutermeister, *Chemistry of Pulp and Papermaking*. 3rd ed., John Wiley, New York, 1941.

[27] C. J. West, *Pulp and Papermaking*. Tech. Assoc. Pulp Paper Ind., New York, 1935–36, 1937, 1938, 1939, 1940, 1941.

[28] C. J. West, *Bibliography of Pulp and Paper Making, 1928–1935*. Lockwood, New York, 1936.

[29] C. F. Cross and E. J. Bevan, *A Text Book of Papermaking*. 4th ed., Spon, London, 1916.

[30] G. S. Witham *Modern Pulp & Paper Making*. 2nd ed., Reinhold, New York, 1942.

paper for packaging and construction, as illustrated by the figures given for United States production in 1940,[31] shows this fact well (Table 4). The "cultural" papers (book, newsprint, and writing grades) comprise but

TABLE 4

PRODUCTION OF PAPER IN THE UNITED STATES IN 1940 (DOBROW[31])

Type of paper	Tons
Paperboard	
Container Board	3,100,000
Box Board	2,900,000
Wrapping paper	2,200,000
Book paper	1,624,000
Newsprint	1,030,000
Writing paper	625,000
Building paper	690,000
Tissue paper	720,000
Other papers	783,000

24% of the total production, and about 29% of the value, produced by the industry. As mentioned below, use of paper sheets in such applications as reinforcements for plastics may widen this industrial market greatly.

8. Fiber Fillers

A recent but highly promising field of application of the natural cellulose fibers comprises their use as fillers and adsorbents. The plastics industry consumes large quantities of purified wood fiber, in finely ground form, to confer greater impact strength and to lower the cost of the phenol-formaldehyde and urea-formaldehyde types of molding compounds. For example, the recent development, by Boyer at the Ford Motor Co.,[32] of the emulsion impregnation of felted-fiber forms with synthetic resins opens the way to future trial and industrial use of this method of fabricating strong, light-weight panels and structural elements. While this development is perhaps a logical continuation of the present-day work with laminated plastic sheets, in which both paper and fabric are impregnated with phenolic-resin coatings, which are then bonded by heat in multiple layers, the potentially lower costs and almost infinite flexibility of the newer techniques make them worthy of mention. The similar developments with resin-bonded plywood, both in sheets and in building-up of formed sections,

[31] M. C. Dobrow, *Paper Trade J.*, **112**, 35 (Feb. 20, 1941).

[32] Anon., *Modern Plastics*, **19**, 38 (Sept., 1941).

as in aircraft shapes[32, 33] illustrate a similar trend with less purified cellulosic fillers. The plywood (so-called plastic) airplane, as exemplified by the DeHaviland "mosquito" bomber, is thus made of laminations, comprising perhaps 90% of wood and 10% of plastic, which, through use of thin sections of wood, as thin as 0.01 in., make maximum use of the strength of cellulose. Other organic fillers for plastics in extensive use today include lignin-enriched or acid-hydrolyzed lignified wood pulp, walnut shell flour, redwood fiber, macerated canvas, and strong rayon or cotton cords, all of which serve specialized uses. High-strength laminates are being made in quantity from Mitscherlich papers impregnated with phenolic resin. The use of wood flours and other cellulose materials as combustible absorbents to hold the nitroglycerin in commercial dynamites[34] also exemplifies a highly useful but little-known application of the retentive and stiffening power of these fibers.

B. REGENERATED CELLULOSE AND RAYON

Regenerated cellulose has been used industrially for at least 60 years. While parchment paper, prepared by submitting paper sheet to the controlled gelatinizing action of concentrated sulfuric acid, and subsequent washing, might be considered an example of this type product, vulcanized fiber sheets comprise a somewhat earlier application of this principle. Extensively used in the latter part of the nineteenth and early twentieth century, because of its hardness, wear-resistance, and good electrical insulating properties, vulcanized fiber has not been expanding in use lately. Its defects, chiefly lack of flexibility and waterproofness, susceptibility to warpage, change of dimension with changes in humidity in the sheet itself, and costly processing (to wash a sheet of fiber ½ in. thick requires daily shifting to wash baths of lower concentration over a period of two months[35]) have led many of the American producers of this material to add the production of laminated phenolic sheet to their lines. Most vulcanized fiber sold today is coated with a water-resisting finish to retard moisture variation. Chief applications of the material lie in making cheaper grades of luggage and carrying cases, electrical insulation, gears, small bearings, washers, etc.

The chief industrial application of the regenerated celluloses is in the familiar rayon field. This development is foreshadowed in Robert Hooke's

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[33] V. Meharg, *Modern Plastics*, **16**, 30 (Oct., 1938); Anon., *Modern Plastics*, **19**, 2 (Oct., 1941).

[34] C. A. Woodbury and W. C. Holmes, *Ind. Eng. Chem.*, **27**, 632 (1935).

[35] F. L. Simons, *Cellulose*, **1**, 105, 130 (1930).

Micrographia" of 1664, in which one finds mention of the possibility of awing "A pretty Kinde of artificial Stuffe" into fibers, to the great profit the drawer. A century later, Reamur suggested that solutions of resins nd gums, such as those used in varnishes, be drawn into threads. How-ver, it was not until 1881 that Hilaire de Chardonnet utilized the first high olymer readily available, nitrocellulose, to carry out these suggestions, rcing a solution of the ester in ether-alcohol through fine glass tubes and

TABLE 5

COMPARISON OF RAYON PROPERTIES

Average for 1925–40 (Avram[36] and Hoff[37])

Fiber	Size, denier	Breaking strength, g./denier		Loss, %	Elasticity, %
		Dry	Wet		
Cuprammonium	150	1.17	0.27	76.5	12.5
Nitrocellulose	150	1.45	0.58	60.2	15.5
Viscose	150	1.26	0.50	60.7	20.0
Acetate	150	1.05	0.59	43.9	..
12-Thread silk	138.8	3.71	3.00	19.1	21
Viscose	300	1.18	0.44	63.0	..
Acetate	300	1.12	0.62	44.4	..

Fiber	Tenacity of fibers, g./denier			Elastic recovery, %	Water absorption at 60% R.H., %
	Dry	Wet	Loss, %		
Silk	4.6	3.9	15.2	50	11
Viscose	1.7	0.9	35.3	30	12
Cordura	3.4	2.1	38.2	40	..
Acetate	1.5	1.0	33.3	50	6.5

ardening the threads in air. The widespread industrial development of this process and the development and expansion of the cheaper and less hazardous viscose and cuprammonium processes are occurrences falling within the memory of most readers, and the technical phases are covered elsewhere in this volume.

It will not be out of place to review here a few of the comparative properties of these rayons[36, 37] (see Table 5) and to mention their competitive places in the industry.

All the regenerated types have essentially the same dry strength, and

[36] M. H. Avram, *Rayon Industry*. Van Nostrand, New York, 1927.

[37] G. P. Hoff, *Ind. Eng. Chem.*, **32**, 1560 (1940).

fall in tenacity to nearly the same extent when wet, with the lowest-denier filaments coming from the nitrocellulose and cuprammonium types. In the United States, nitrocellulose rayon production never amounted to more than 10 million pounds annually, while in 1940 there were produced about 12 million pounds of cuprammonium rayon, 245 million pounds of viscose rayon, and 133 million pounds of acetate rayon. Production of Chardonnet rayon was discontinued in the United States in 1935 because of the competition and the labor situation, and the plant was moved to Brazil. The nitrate process, in addition to the hazard involved in handling flammable solvents and nitrocellulose, produced only two-thirds the weight of finished yarn as was spun, due to contraction in weight on denitrating. Although this produced thin fibers, costs of the raw materials remained static while the material costs in the viscose and acetate processes became progressively lower; hence the material became noncompetitive. The acetate rayons, because of better wet strength, are taking a larger share of this market in spite of somewhat higher costs. All these rayons may be made into staple fibers, which in the United States amounts to about 15% of the annual total of the filament spun. The world production of rayon filament in 1940 was about 1150 million pounds, and of staple, about 1300 million pounds. The sudden rise in world production of staple began in 1934 as a result of the efforts of totalitarian countries to develop wool substitutes.[38] It is unlikely that the United States development of rayon staple will reach any such scale. The trend in this country seems to be in the direction of fiber from casein or soybean proteins for such purposes, as well as for hat felts, etc. Raw silk shortages encountered in this country as a result of the stoppage of overseas supply are being met by development of high-strength cuprammonium and acetate rayon yarns, as well as by the polymers of adipic acid and hexamethylenediamine (nylon). *World production of rayons* in 1940 was 2381 million pounds, accounting for 13% of world production of fibers (cotton, 74%; wool, 12%; silk, 1%).

Products allied to the rayon types of regenerated cellulose include transparent wrapping sheet (cellophane), sausage casing, cellulose caps and bands for packages, cellulose sponge, and bottle seals These are chiefly derived from viscose. All the uses of the regenerated celluloses stem from the fact that by these processes the shape and color of the cellulose can be exactly controlled while enough of the strength and toughness of the cellulose is retained to resist the wear of these fiber or packaging applications. In the rayons, the loss of tensile strength due to a lower D.P. as described

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[38] Anon., *Chem. & Met. Eng.*, **48**, 106 (Feb., 1941).

in Chapter IX, Section G, 3, is apparently largely offset by the longer fiber As a matter of fact, the rayon processes also permit control of fiber fineness, uniformity of staple, porosity, and luster, making five of the nine important fiber properties under mechanical or chemical control.

C. CELLULOSE DERIVATIVES

In describing the technical applications of the cellulose derivatives, it seems advisable to present the subject from the viewpoint of the industry involved, rather than from that of the specific cellulose derivative. It is believed that the approach of present-day technologists to the question of raw materials for any given industry is along this line and involves a comparison of properties of various materials available to do a given job. While much of the formal order of the chemical classification may be sacrificed by such an arrangement, it is believed that the comparison of materials and reasons for their present use in various fields can be most effectively developed in this manner.

A comparison of the properties of commercially available cellulose derivatives is shown in Table 6.[39] Upon this wide variation in properties with substituent and degree of substitution is founded the widespread use of the cellulose derivatives (see Table 7).

1. Protective Coatings

With cellulose nitrate the first recorded cellulose derivative, it is only natural that it should have been the first to be used in protective coatings. Maynard in 1847 proposed the use of ether-alcohol solutions of nitrocellulose as surgical dressings, the present-day collodion. A history of the development of lacquer shows how it took a combination of readily available solvents and nitrated cotton, the unprecedented expansion of the automobile industry, and improvements in the control of the viscosity or chain length of the cellulose nitrate, to bring cellulose lacquers into prominence as flexible, mass-production finishes.[40] Other cellulose derivatives, notably the acetate, acetate propionate, acetate butyrate, and the ethyl ethers, are finding increased usage in the protective-coating field, either as the main film-forming material or in combination with synthetic resins. The chief protective-coating uses of the cellulose derivatives may be subdivided into lacquers, fabric coating, paper coating, adhesives, and varnish bodying.

These widespread uses of cellulose derivatives have their origin in the

[39] Table 6 is based on data from the booklet *Ethyl Cellulose*. Hercules Powder Co., Wilmington, Del., 1940.

[40] D. R. Wiggam and W. E. Gloor, *Ind. Eng Chem.*, **26**, 551 (1934).

TABLE 6—PROPERTIES AND TYPES OF CELLULOSE DERIVATIVES OF INDUSTRIAL IMPORTANCE[39]

	Nitrocellulose	Cellulose acetate	Ethylcellulose, N-type	Cellulose acetate butyrate, lacquer-type	Cellulose acetate propionate, lacquer-type
GENERAL PROPERTIES					
Form	White fibers	White flakes	White granules	White flakes	White flakes
Color (Film)	Water-white	Water-white	Water-white	Water-white	Water-white
Odor	None	None	Slightly musty to none	Slight to none	None
Clarity (Film)	Excellent	Excellent	Good	Good	Good
Taste	None	None	Slight to none	None	None
PHYSICAL PROPERTIES OF SOLIDS					
Bulking Value (in soln.), gals./lb.	0.0704	0.0847	0.1035	0.0907	0.0908
Specific Vol. (in soln.), in.^{3}/lb.	16.26	19.57	23.91	20.95	20.97
Specific Gravity (Cast Film)	1.58	1.36	1.14	1.29	1.29
Index of Refraction (Principal)	1.514	1.48	1.47	1.47	1.47
Ultraviolet Transmission	Transmits down to 3130 Å. (absorbs sunlight)	Transmits down to 2650 Å. (passes sunlight)	Transmits down to 2800 Å. (passes sunlight)	Transmits down to 2650 Å. (passes sunlight)	Transmits down to 2800 Å. (passes sunlight)
ELECTRICAL PROPERTIES OF UNPLASTICIZED FILMS					
Specific Surface Resistivity, ohms	....	15×10^{10}	20×10^{12}	20×10^{12}	10×10^{12}
Dielectric Strength (A.S.T.M. Method), volts/mil	....	1400	1500	1900	1400
Dielectric Constant:					
25°C.—1000 cycles	....	5.7–7.0	3.9	4.5	5–6
25°C.—60 cycles	....	...	2.6	...	...
Power Factor:					
25°C.—1000 cycles	....	0.0050	0.0025	0.0048	0.005
25°C.—60 cycles	....	...	0.0030	...	...
Electric Charge (on	Negative	Positive	Positive	Positive	Positive

kg./cm.^{2}					
Breaking Load (Wet), kg./cm.^{2}	90% dry strength	450–600	80–85% dry strength	250–480	80% dry strength
Elongation (Dry), %	10–28	7–10	10–40	3–12	4–18
Elongation (Wet), %	10–34	10–15	11–16	2–25	3–12
Modulus of Elasticity, lbs./in.^{2}	2.8×10^5	2.12×10^5	1.89×10^5	2.01×10^5	1.74×10^5
Flexibility, Schopper					
Double Folds:	0.0035-in. film	0.0022-in. film	0.004-in. film	0.0025-in. film	0.004-in. film
Original	5–60	20–60	60–100	0–45	3–20
Irradiated with direct mercury vapor arc	0 (2 hrs.)	2–10 (1 hr.)	10–55 (1 hr.)	0–0.5 (1 hr.)	0–10 (6 hrs.)
Hardness Index, Sward Rocker, % of glass	90%	78%	71%	78%	76%

THERMAL PROPERTIES OF UNPLASTICIZED FILMS

Burning Rate, (0.001-in. film)	5–10 in./sec.	1.3 in./sec. (similar to newsprint)	1–2 in./sec. (sometimes snuffs out)	<1.0 in./sec. (sometimes snuffs out)	<1.0 in./sec. (sometimes snuffs out)
Effect of Dry Heat	Slow decomposition at 135°C.	No discoloration at 180°C., 1 hr.	Retains flexibility after 72 hrs. at 100°C.	No discoloration at 180°C., 1 hr.	No discoloration at 180°C., 1 hr.
Melting or Softening Point	Decomposes	56% combined acetic acid type: 240–260°C. 53% combined acetic acid type: 235–245°C. 51% combined acetic acid type: 250–270°C.	T-Type: 160°C. N-Type: 135°C. K-Type: 145°C. G-Type: 160°C.	Lacquer-Type: 215–225°C. Plastics-Type: 180–190°C.	200–210°C.

TABLE 6—PROPERTIES AND TYPES OF CELLULOSE DERIVATIVES OF INDUSTRIAL IMPORTANCE[39] (*Continued*)

	Nitrocellulose	Cellulose acetate	Ethylcellulose, N-type	Cellulose acetate butyrate, lacquer-type	Cellulose acetate propionate, lacquer-type
PHYSICAL-CHEMICAL PROPERTIES OF UNPLASTICIZED CLEAR FILMS					
Effect of Sunlight:					
Discoloration	Considerable	Very slight	Very slight	Very slight	Very slight
Embrittlement	Considerable	Very slight	Very slight	Very slight	Very slight
Effect of Aging	Slight	Very slight	Very slight	Very slight	Very slight
Effect of Water:					
Hot	Nil	Slow hydrolysis	Nil	Slight	Slight
Cold	Nil	Very slight	Nil	Very slight	Very slight
Water Absorption (80% R.H., for 24 hrs. at 21°C.)	1.0%	4.9%	2.0%	1.0%	1.5%
Moisture Vapor Permeability (21°C.), g./cm.²/0.01 cm./hr.	2.8×10^{-4}	8.4×10^{-4}	6.4×10^{-4}	6.2×10^{-4}	7.3×10^{-4}
General Resistance to:					
Acids:					
Weak	Fair	Fair	Fair	Fair	Fair
Strong	Poor	Poor	Poor	Poor	Poor
Alkalies:					
Weak	Poor	Poor	Excellent	Fair	Poor
Strong	Poor	Poor	Excellent	Poor	Poor
Solubility in:					
Alcohols	Partly soluble	Swollen	N- and G-Type: soluble	Swollen	Swollen
Ketones	Soluble	Soluble in lower ketones	Soluble	Soluble in lower ketones	Soluble
Esters	Soluble	Soluble in lower esters	Soluble	Soluble in lower	Soluble

Hydrocarbons:					
Aromatic	Swollen	Swollen	Soluble	Swollen	Swollen
Aliphatic	Insoluble	Insoluble	N-Type: swollen G-Type: insoluble	Insoluble	Insoluble
Oils:					
Mineral	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
Animal	Insoluble	Insoluble	Swollen and softened	Insoluble	Insoluble
Vegetable	Insoluble	Insoluble	Swollen and softened	Insoluble	Insoluble
Typical Solvents	Esters and ketones through 5–6 carbon homologs, alcohols, alcohol-ethers	Lower esters and ketones, chlorinated hydrocarbons with alcohol	Alcohols, esters, ketones, aromatic and chlorinated hydrocarbons, ethers, organic acids	Lacquer-Type: Lower esters and ketones, chlorinated hydrocarbons with alcohol Plastics-Type: butyl acetate	Ketones, esters, toluene-alcohol, chlorinated hydrocarbons
Compatible Resins (Types)	Nearly all types	Sulfonamide - formaldehyde, Vinsol, benzoic - modified alkyds, 100% phenolics, glycol phthalates	Many natural resins, phenolic- and resin acid - modified alkyds, resin acids and their esters, nonhardened phenolics	Sulfonamide - formaldehyde, Vinsol, benzoic - modified alkyds, 100% phenolics, glycol phthalates; also dammar, acrylics, vinyl acetates, acetal resins	Sulfonamide - formaldehyde, Vinsol, benzoic - modified alkyds, 100% phenolics, glycol phthalates; also dammar, acrylics, vinyl acetates, acetal resins; also Petrex 5
Plasticizers (Types)	Nearly all, including oils	Methyl to butyl ester plasticizers, no oils	Nearly all, including oils	Nearly all chemical plasticizers, no oils	Nearly all chemical plasticizers, no oils
Compatible Waxes (Types)	None	None	Coal tar, stearin pitch, Gilsonite, fatty alcohols, all waxes except petroleum hydrocarbons	None	None
Compatible Cellulose Derivatives	Acetate, mixed esters, ethylcellulose	"RS" $^1/_2$-sec. nitrocellulose	Nitrocellulose in all proportions	Nitrocellulose, acetate propionate	Nitrocellulose, acetate butyrate

TABLE 7

PROPERTIES AND TYPES OF CELLULOSE DERIVATIVES OF INDUSTRIAL IMPORTANCE CLASSIFIED ACCORDING TO USES

Cellulose derivative	Composition	Substitution	Viscosity
	PROTECTIVE COATINGS		
Nitrocellulose	"RS": 12.0% nitrogen	2.26	10–25 cps.; 1/4, 1/2, 5–6, 15–20 sec.
	"AS": 11.5% nitrogen	2.11	1/2, 30–40 sec.
	"SS": 10.8% nitrogen	1.92	1/4, 5–6 sec.
Cellulose Acetate	54–56% combined acetic acid or 38.7–40.1% acetyl	2.35–2.48	2–6, 18–30 sec.
Cellulose Acetate Butyrate	27–32% acetyl; 15–19% butyryl	1.9–2.2; 0.6–0.8	1–5, 10–25, 30–45 sec.
Cellulose Acetate Propionate	13–15% acetyl; 30–34% propionyl	0.8–1.1; 1.6–1.8	1–6, 12–24, 30–60 sec.
Ethylcellulose	T: 48.5–50% ethoxyl	2.5–2.58	10–300 cps.
	N: 46.8–48.5% ethoxyl	2.41–2.5	7–300 cps.
	K: 45.5–46.8% ethoxyl	2.35–2.41	14–200 cps.
	G: 44.5–45.5% ethoxyl	2.29–2.35	22–200 cps.
	PLASTICS		
Nitrocellulose	11.0 ± 0.2% nitrogen	2.0	25 sec. and higher
Cellulose Acetate	52.5–54% combined acetic acid or 37.6–38.7% acetyl	2.2–2.35	20–120 sec.
	56–58% combined acetic acid or 40.1–41.6% acetyl	2.48–2.62	30–250 sec.
Cellulose Acetate Butyrate	14% acetyl; 36% butyryl	1.0; 1.6	10–40 sec.
Cellulose Acetate Propionate	13–15% acetyl; 30–34% propionyl	0.8–1.1; 1.6–1.8	above 300 cps.
Ethylcellulose	N: 46.8–48.5% ethoxyl	2.41–2.5	above 100 cps.
	K: 45.5–46.8% ethoxyl	2.35–2.41	above 100 cps.
	G: 44.5–45.5% ethoxyl	2.29–2.35	above 50 cps.
	RAYON		
Nitrocellulose	11–12% nitrogen	2.0–2.26	50 sec. and higher
Cellulose Acetate	53.5–55% combined acetic acid or 36.3–39.4% acetyl	2.3–2.4	50–100 sec.

TABLE 7 (*Continued*)

PROPERTIES AND TYPES OF CELLULOSE DERIVATIVES OF INDUSTRIAL IMPORTANCE CLASSIFIED ACCORDING TO USES

Cellulose derivatives	Composition	Substitution	Viscosity
	FILM		
Nitrocellulose	12.0% nitrogen	2.26	20 sec. and higher
Cellulose Acetate	55.5–56.5% combined acetic acid or 39.8–40.5% acetyl	2.45–2.5	25 sec. and higher
Cellulose Acetate Butyrate	19% acetyl; 27% butyryl	1.3; 1.1	100 sec.
Cellulose Acetate Propionate	14% acetyl; 32% propionyl	0.95; 1.65	above 300 cps.
Ethylcellulose	N: 46.8-48.5% ethoxyl	2.41–2.5	above 100 cps.
	K: 45.5–46.8% ethoxyl	2.35–2.41	above 100 cps.

nature of the materials as lyophilic colloids, which will swell and then disperse to a homogeneous, viscous solution when treated with one or more times their weight of the proper volatile solvent liquid. By application of the solution to the surface to be protected, the volatile solvent evaporates, depositing the protecting film in intimate contact with the surface. In such solutions other compounding agents may be added to modify the properties of the finished film, pigments and dyes may be dispersed to add opacity and color to the film, and cheaper solvents and diluents may also be added. In speaking of these technical "solutions" it should be borne in mind that they are viscous colloidal dispersions of the film-forming ingredients. As colloidal dispersions, they are much more concentrated than the ideal sol used by Staudinger in molecular-weight studies, since in the quest for economy it is necessary to use as little solvent as possible to disperse the cellulose derivative. For practical use of the solutions, the empirically determined viscosity-concentration curves[41, 42] (see also Fig. 8 of Chapter VIII, Section B, p. 661) and blending charts based on the Arrhenius relation are chiefly used[42, 43] (see also Fig. 50 of Chapter IX, Section F, p. 975). The system of K-values described by Fikentscher[44] is used by I. G. Farbenindustrie in characterizing its nitrocellulose.[45]

Films laid down from such solutions may be sprayed, dipped, brushed

[41] E. P. Irany, *J. Am. Chem. Soc.*, **60**, 2106 (1938).
[42] *Nitrocellulose Handbook*. Hercules Powder Co., Wilmington, Del., 1939.
[43] *Ethocel*. The Dow Chemical Co., Midland, Mich., 1940.
[44] H. Fikentscher, *Cellulosechem.*, **13**, 58 (1932).
[45] *Collodiumwolle*. I. G. Farbenindustrie, Frankfort (Main), 1931.

roller-coated, padded, or applied with a doctor knife, depending on the usage. In fact, the only limitations are those imposed by the requirements of easy solvent removal, character of the film desired, and ability to control the drying atmosphere.

(*a*) *Lacquers*

During the last 20 years, the use of the lacquer finishes, broadly defined as coatings in which nitrocellulose or other cellulose derivative forms the base, and which dry by evaporation without chemical change, has expanded widely. Tough and durable enough to deserve the same name as their

TABLE 8

USE OF NITROCELLULOSE IN LACQUERS[46]

Year	Total of enamels, clears, dopes, and thinners, in gallons
1942	49,441,510
1941	64,504,681
1940	47,969,129
1939	42,782,431
1938	34,437,922
1937	46,817,113
1936	44,287,268
1935	36,497,411

oriental counterparts based on urushiol and other materials, their use became widespread because of the demand of mass-production industry for a fast-drying coating that could match the pace of the production lines. The first large use of "pyroxylin" lacquers, based on nitrated cellulose, was made by General Motors Corporation on the 1923 model Oakland automobile, and within five years the durability of the finish, speed of drying, wide color variety available, and economy of the coating operation had put nitrocellulose finishes on almost all motor vehicles made the world over. These lacquers, applied by spraying, became possible through the development of a lower-viscosity cellulose nitrate which would give a solution of viscosity less than 70 centipoises (the limit for the first spray guns), yet which would have a concentration more than 10% of nitrocellulose, together with additional resins, plasticizers, and pigments. That the use of cellulose nitrate in lacquers is an important and continuing factor in American industry is shown in Table 8.[46]

[46] From U. S. Dept. Commerce reports on lacquer sales.

Other than nitrocellulose, the film ingredients of commercial lacquers usually include:

(1) *Plasticizers*, which may be classified as solvent types, including camphor, dibutyl phthalate, tricresyl phosphate, butylphthalyl butyl glycolate, and a number of other organic esters; and nonsolvent types such as refined castor oils, blown oils, and oil derivatives. The solvent-type plasticizers apparently form a uniform dispersion or solid solution of the nitrocellulose, which generally becomes stiffer at low temperatures,[47] while the nonsolvent-type, giving films with plasticizer-rich and plasticizer-poor regions, generally produce films with better flexibility at low temperatures.[48] Both types of plasticizers are aptly described by the German term *Weichmachungsmittel* (softeners), since they decrease the tensile strength and increase the elongation of films containing them. They are usually liquids of low vapor pressure, minimum water solubility, and minimum tendency to hydrolyze or interact with nitrocellulose to promote decomposition.

(2) *Resins*, which tend to harden the film, promote gloss and water resistance, and build up the solids content of the film. Natural resins such as Batavia dammar have been widely used; also, derivatives of natural resins such as the glycerol and glycol esters of rosin, as well as a host of oil- and acid-modified phthalic and maleic condensation resins are finding wider and wider usage. While many resins tend to reduce the cost of lacquer solids, yet their proper use with relation to the other ingredients may enhance light and weather resistance, resistance to low temperatures, and gloss.

(3) *Pigments*, which give color to the film and improve its hiding and weathering qualities. Zinc oxide and titanium whites, carbon black, chrome yellows, Chinese blues, and Lithol and other toners are usually found in lacquers. To get fine grinding of the pigment so as to make the most effective use of it, it is often dispersed, by use of stone or roller mills, in the plasticizer used in the formula. Pigment may also be ground in the nitrocellulose solution in ball or pebble mills. Another effective way of grinding pigment into a lacquer formula is to mill it with a portion of the nitrocellulose and plasticizer in a Banbury mixer or a two-roll mill. The matching of colors and holding production batches true to shade is one of the arts highly essential to lacquer production. The use of aluminum bronze pigments gives iridescent finishes of particularly good weather resistance.

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[47] E. Ott, *Ind. Eng. Chem.*, **32**, 1641 (1940).
[48] O. Kratky, *Kolloid-Z.*, **70**, 14 (1935).

While these ingredients play important parts in the success of the lacquer finishes, the most important role is that of the cellulose nitrate itself. The only high-polymeric material present, it provides the tough framework which holds together the other ingredients. The early brass and metal lacquers were based on nitrocellulose of viscosity higher than 5 seconds, while the expansion of spray lacquers was based on the discovery that material of half-second viscosity would give very practical finishes.[49] With the realization that in natural cellulose one is dealing with a material that occurs in a high degree of polymerization in nature, and that most technical processes tend to shorten these polymers,[50] efforts were made to utilize still lower polymers. It was soon found that the film-forming properties and tensile strengths of these lower-viscosity materials dropped off sharply below about D.P. 100 in the nitrocelluloses, and that cold check resistance of lacquers based on them became noticeably less. However, for some industrial purposes, material with very low D.P. (10-cp.-type nitrocellulose) finds application, although these materials are most useful in the softer formulations.[51] The utility of these lower-viscosity materials is of particular importance in view of the demand for higher-solids lacquers to meet the competition offered by some of the alkyd resins in this field.

Development of the continuous digestion process by Milliken[52, 53] made it practical to produce these very low-viscosity types of nitrocellulose commercially. (See also Chapter VIII, B.)

The other important variable in nitrocellulose in addition to viscosity is nitrogen content. The types of nitrocellulose most widely used in lacquers contain about 12% nitrogen. Exploration of the range of soluble lower nitrates of cellulose indicated that for best outdoor weathering, material of from 11.5 to 12.3% nitrogen content gave the best results. The materials of lower nitration were more water sensitive and allowed the water to penetrate the protective film faster. Since the decomposition of the nitrocellulose lacquer under weathering tends to denitrate and to depolymerize the outer layers of the coating, this is understandable.[51] Materials of higher nitration, becoming less soluble and more flammable as the esterification increases, are of less interest to the coating trade. Analysis of a typical nitrocellulose used in the lacquer industry is given in Table 9.

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[49] E. M. Flaherty, U. S. Patent 1,629,999 (May 24, 1927).

[50] C. Ellis, *Ind. Eng. Chem.*, **28**, 1130 (1936).

[51] W. E. Gloor, *Ind. Eng. Chem.*, **27**, 1162 (1935).

[52] M. G. Milliken, *Ind. Eng. Chem.*, **22**, 326 (1930).

[53] M. G. Milliken (to Hercules Powder Co.), U. S. Patent 1,818,733 (Aug. 11, 1931); Hercules Powder Co., British Patents 301,267 (Feb. 23, 1928); 338,941 (May 29, 1929).

TABLE 9

ANALYSIS OF A TYPICAL LACQUER-GRADE NITROCELLULOSE[54]

% Nitrogen:	12.00 ± 0.10% dry basis
Viscosity:	3 to 4 secs., $^5/_{16}$-in. steel ball, 20% dry basis in solvent comprising 55 parts toluene, 25 ethanol, 20 ethyl acetate; 10-in. fall through 1-in. cylinder at 25°C.
Volatile Content:	35% as shipped, usually denatured alcohol
Stability:	25 mins. or more German Test[a] (methyl violet at 134.5°C.).

[a] A 2.5-g. sample of air-dried nitrocellulose is placed in the bottom of a 12-in. test tube f $^3/_4$ in. diameter. The tube is closed with a stopper from which a methyl violet paper s suspended, and placed in a bath kept at 134.5°C. The time required to completely ischarge the violet color of the test paper is noted as the stability time or "German Test" in minutes.

Other alcohols, such as isopropanol, *n*-butanol, and Pentasol (a mixture of amyl alcohols), have been used to wet nitrocellulose for special purposes. Such wetting is necessary to avoid the hazards which arise when handling dry nitrocellulose. Fractionation of these lacquer-type nitrocelluloses reveals that they are uniformly nitrated within 0.2% nitrogen, but that a wide range of viscosity fractions occurs in the material.[55] While it appears that a narrower range of viscosity distribution about the average would give a little stronger material, the cost of doing this seems far greater than the improvement would warrant, and a wide viscosity distribution seems to favor adhesion to surfaces.

The cellulose used for the manufacture of lacquer types of nitrocellulose has been in the past mainly obtained from cotton linters. The method devised by Stern[56] for preparing wood pulp cellulose for nitration has made it possible to use this type of cellulose effectively, thus widening the available raw material sources.

The economy of the lacquer business requires a large supply of cheap volatile solvents: these include butanol and butyl acetate from the Weizmann fermentation of sugars; amyl alcohols and esters from the chlorination of natural gas hydrocarbons and hydrolysis of the product; ethanol; ethyl acetate; and diluents such as toluene and petroleum frac-

[54] Am. Soc. Testing Materials, *Tentative Standards*, D 301–31 T; see A.S.T.M. *Standards*, D 301–33, for details.

[55] H. M. Spurlin, *Ind. Eng. Chem.*, **30**, 538 (1938).

[56] R. L. Stern (to Hercules Powder Co.), U. S. Patent 2,028,080 (Jan. 14, 1936); Hercules Powder Co., British Patent 463,437 (June 24, 1937).

tions. Combinations of these, of maximum solvency and minimum cost, may be selected by the methods outlined by Hofmann and Reid,[57] Doolittle,[58] and Ware.[59]

Nitrocellulose lacquers are used on airplanes, automobiles, and furniture, as well as on many industrial jobs for colored finishes for metal; also as clear finishes for brass and copper, and as dip coatings for brush handles, toys, hardware, novelties, hats, and other such mass-production items. In general, outdoor application of lacquer is restricted to metal surfaces, which must be carefully prepared. The metal may be cleaned with zinc and manganese phosphate solution, which deposits a coating of secondary ferrous phosphate and manganese phosphate to which the coating can adhere.[60] A rust-resisting primer (frequently based on oil) is then applied. This may be baked, often with infrared lamps.[61]

Large irregularities in the surface are filled with a glazing compound and a heavy coat of a surfacer is then applied, which when dry is thoroughly sanded. The object of the surfacer is to fill the scratches and rough spots and to build up as nearly as possible a perfectly level surface. On this prepared surface a lacquer coat may be applied, sanded, another coat applied and sanded, and a final coating sprayed on. This final coat, after sanding, is mist-coated and polished. Such a schedule requires considerable labor, but produces a beautiful finish. It is necessary because the lacquer spray coats must be applied to a smooth surface to avoid the pebbled appearance known as orange peel, since successive coatings on an irregular surface tend to accentuate the irregularities originally present. Such a coating, applied in a workmanlike manner, will last for a decade even under adverse weather exposure. Efforts to reduce the sanding required and the number of coats have been made. These have included use of solvents giving better flow-out, higher-solids lacquers requiring only two spray coats instead of three to apply the coating of 1.5 to 2 mils required, and spraying of hot lacquers of higher solids, heated to lower their viscosity to a sprayable consistency.[62, 63, 64] These efforts have been partly successful. Another economy has been the recovery of

[57] H. E. Hofmann and E. W. Reid, *Ind. Eng. Chem.*, **20**, 431 (1928).

[58] A. K. Doolittle, *Ind. Eng. Chem.*, **27**, 1169 (1935); **30**, 189 (1938).

[59] V. W. Ware and W. O. Teeters, *Ind. Eng. Chem.*, **31**, 378, 1118 (1938); V. W. Ware and W. M. Bruner, *Ind. Eng. Chem.*, **32**, 78, 519 (1940).

[60] V. M. Darsey, *Ind. Eng. Chem.*, **33**, 222 (1941).

[61] J. L. McCloud, *Ind. Eng. Chem.*, **33**, 225 (1941).

[62] C. Bogin, *Paint Oil Chem. Rev.*, **103**, 7 (July 17, 1941); **103**, 7 (July 31, 1941).

[63] J. B. Wiesel, *Paint Oil Chem. Rev.*, **103**, 111 (Nov. 14, 1941).

[64] Commercial Solvents Corp., British Patent 527,729 (Oct. 15, 1940).

acquer solids from the over-spray[65] by water washing the exhaust from the pray booth and collecting the precipitated lacquer solids. Solvent recovery rom spray booths has not proved practical. Lacquer finishes for wood xposed outdoors have not been too successful, but on furniture used ndoors, lacquers offer the most readily applied, tough finish. Large objects ike automobile panels and furniture are usually sprayed, smaller metal arts and wooden-ware items are most often dip-coated. In the past dec-de, the outstanding success of the spray lacquers in industrial work led o many efforts to apply lacquers by brushing. This was especially evident n the shelf goods finishes, where many manufacturers offered lines for ublic consumption. The chief difference between these brushing lacquers nd the spray lacquers was that higher-boiling solvents and higher-solids ontents were used. The difficulty with most of these finishes was that he user had to be an expert in order to apply a reasonably smooth coat vith them. The flow of the formulas, especially when applied on vertical urfaces, often caused sagging.

The Cellulose Ester Subcommittee of the Protective and Technical Coat-ngs Defense Industry Advisory Committee of WPB issued some interesting tatistics concerning the place of nitrocellulose lacquers in the American inishing industry. Over the period from 1938–1940 the percentage of acquer in total industrial sales of paint, varnish, and lacquer ranged from 27.3 to 30.2%, with an average nitrocellulose content ranging from 1.05 to 0.96 lbs. per gallon of lacquer. Esselen[66] states that, in 1927, 1.46 lbs. of itrocellulose were used per gallon. The variation is attributed to more extensive use of other solids-building ingredients in the film.[63]

While coating technologists find nitrocellulose the easiest cellulosic raw material to formulate because of its wide range of solvents and compatible ngredients, its sensitivity to light, heat, and flammability preclude its use n applications where extreme color fastness or heat resistance is required. Efforts were made to use cellulose acetate finishes for such purposes, either as the whole lacquer base or as a protecting topcoat,[67] but these were not practical because of the poor durability of the cellulose acetate finishes, due to their natural water permeability, and the lack of compatible modifiers to improve this condition.

To improve these properties of the finishes, the light- and heat-resisting cellulose mixed esters (either the acetate butyrate or acetate propionate)

[65] S. G. Saunders, *Ind. Eng. Chem.*, **33**, 230 (1941).

[66] G. J. Esselen, *Ind. Eng. Chem.*, **26**, 26 (1934).

[67] N. S. Kocher (to Eastman Kodak Co.), U. S. Patents 1,958, 706–8 (May 15, 1934)

were tried because of better water resistance, solvent range, and compatibility with resins and plasticizers. While lacquer formulas based on these materials have properties approaching those of the nitrocellulose lacquers, for many applications on metal or wood they are too costly. However, these materials are being used with some success in clear metal finishes for outdoor exposure. Good results have been obtained with such finishes as clear coatings for architectural aluminum,[68] as well as on aircraft wings. Costs of lacquers based on these mixed esters have been high not only because of their own inherent price, but because they do not tolerate diluents as well as nitrocellulose, and hence require more of the expensive ester solvent. However, it is conceivable that, with increasing production of these esters for plastics, it will be possible to make the more soluble esters with greater proportions of higher acyl content[69] more cheaply. To all appearances, though, their use in the field of protective lacquers for solid objects will continue to be minor.

The introduction of ethylcellulose into the protective coatings field has created such widespread interest as to cause it to be regarded as the cellulose material of the future. Its wide compatibility with resins, oils, and plasticizers, and easy solubility in solvents, makes it more like nitrocellulose in these respects than any of the other cellulose derivatives available. Recent figures indicate a usage of about 4 million pounds yearly in the United States for finishes.[63] Slow-burning and light-resistant, ethylcellulose also has the property of remaining flexible at temperatures as low as $-70°C$. As a result, ethylcellulose is being used in lacquers either alone or in combination with nitrocellulose to improve resistance to cracking of the finish when exposed to rapid variation in temperature. As such, furniture and ignition cables for automobiles and aircraft motors have been most active fields for the development of ethylcellulose finishes. It is said that this cold flexibility results from increasing solubility of the ether in plasticizer at low temperatures.

Application of this fact is reflected in efforts to provide a more cold-resisting artificial leather by using mixtures of ethylcellulose with nitrocellulose as the coating base,[70] by using ethylcellulose coatings for wooden or fabric aircraft surfaces to give a smooth aerodynamic surface and a temperature-resisting, tough coating,[71] and by using ethylcellulose in mak-

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[68] *Hercose C in Clear Metal Lacquers.* Hercules Powder Co., Wilmington, Del., 1937.

[69] C. R. Fordyce, M. Salo, and G. R. Clarke, *Ind. Eng. Chem.*, **28**, 1310 (1936).

[70] P. F. Robb (to Hercules Powder Co.), U. S. Patent 2,290,072 (July 14, 1942).

[71] L. Pereny and G. A. Meisinger, U. S. Patent 2,287,484 (June 23, 1942).

ng clear lacquers to render glass shatterproof.[72] Other applications of thylcellulose lacquers which make use of its wide miscibility with resins nclude: as a vehicle for luminous paints, in combination with low-acid-umber maleic-modified ester gums; as a toughener for rosin or rosin ster in the production of shellac substitutes, using the alcohol-soluble 8% ethoxyl variety; as an impregnant to make fabric impermeable to mus-ard gas, when properly formulated with oils; and in coating rubber articles o impart gloss and reagent protection. Being compatible with a wide ariety of soft resins, such as sebacic acid esters or butyl stearates, ethyl-ellulose can be formulated to have very good adhesion to porous paper or extile surfaces; while on hard, nonporous surfaces, use of rosin-modified henolics or maleic ester gums with ethylcellulose provides adhesion. The outstanding alkali resistance provided by ethylcellulose finish is ex-mplified by its use, together with amylnaphthalene as the softening modi-ier, in lining the tank cars used in shipping strong sodium hydroxide solu-ions.[73]

In general, the present industrial scene shows almost an equilibrium stablished between the market for cellulose lacquers on the one hand, nd the finishes made from oils and synthetic resins, which dry by oxida-ion or polymerization, on the other. The cellulose lacquers have the remendous general advantages of being adaptable to any scale of produc-ion; of rapid drying which requires small investment for drying equip-nent; of ease of application which leads to a very low percentage of im-erfect finished pieces: and of offering a wide variety of protective films.

(*b*) *Coated Textiles*

In this field, the volume use of nitrocellulose remains quite high. The asic process of the industry comprises the application of a solution which vill deposit a supple and flexible film on the cloth. By careful compound-ng of a higher-viscosity nitrated cellulose with various treated castor oils, nd applying several coats of decreasing flexibility to specially woven louble-filled cotton fabrics, large amounts of quite durable artificial eathers are produced, leathers which will withstand more than a million louble folds.[74] The D.P. of the nitrocellulose used for this purpose is

[72] W. W. Koch, *Modern Plastics Catalog.* Plastics Catalogue Corp., New York, 1943, . 752.

[73] W. F. Waldeck (to Pittsburgh Plate Glass Co.), U. S. Patent 2,111,342 (Mar. 15, 938); I. E. Muskat (to Pittsburgh Plate Glass Co.), U. S. Patent 2,162,027 (June 13, 939).

[74] D. McBurney, *Ind. Eng. Chem.*, **27**, 1400 (1935).

quite high, about 250 to 400, yet fairly concentrated dispersions are applied, with a solids content of 30 to 40%; because the solutions are heavily pigmented, the oils are present in quantities greater than the nitrocellulose, and the coating equipment can apply solutions of viscosity approaching 1000 poises in uniform layers. Variations of the technique are used in coating cloth for window shades, washable wall cloths, and glazed chintzes. Screen printing, a process by which a design blocked out in silk bolting cloth may be transferred in reverse to a surface beneath, is also used in applying designs to cloth and paper, the color base usually being a lacquer because of fast, low-temperature drying.

A fascinating chapter in the story of the application of cellulose finishes to fabric lies in their use as aircraft dopes.[75] The early military aircraft of the first World War had the fabric wings stiffened with nitrocellulose dopes to hold the airfoil surfaces more exactly. Experience showing these to be too flammable when hit with tracer bullets, cellulose acetate dopes were used in their place. Despite production difficulties, and early troubles in the finishing plants, where the large-scale use of tetrachloroethane as a solvent caused several deaths among workmen who inhaled the vapors,[76] proper solvents were worked out to permit most of the Allied machines to be coated with cellulose acetate finishes at the time of the Armistice. The cellulose acetate manufacturing equipment left on hand at that time produced the incentive which led to the rapid commercialization of acetate rayon in the twenties.

During the two decades of peace, the small commercial airplane industry went back to nitrocellulose dopes for aircraft with fabric wings, and the development of the all-metal plane, which needed no protection, seemed to presage that the cellulose lacquers would be largely out of the air. However, the use of aircraft based on ocean-going carriers made consideration of flammability, weight, and space important, and search was continued for a good aircraft dope to be used on fabric-covered planes for this purpose,[75] and also for the lighter-than-air dirigibles. On seaplanes based in tropical ports, trial of cellulose acetate dopes was discontinued after it was found that the wing coverings became slack after the plane had been left exposed to the humid night air, and nitrocellulose dopes were retained because of their superior water resistance. The benzyl and ethyl ethers of cellulose were suggested, but widespread adoption was not forthcoming, probably because of the poor weather resistance of the early commercial

[75] G. M. Kline, *Ind. Eng. Chem.*, **27**, 556 (1935).

[76] A. Hamilton, *Industrial Poisons in the United States*. Macmillan, New York, 1925, pp. 445–7.

roducts, and because of their cost. Use of the higher-acetylated types f cellulose acetate,[77] and of cellulose acetate butyrate and cellulose cetate propionate, as cellulose organic esters whose water resistance approached that of cellulose nitrate, became more practical,[78] and in the resent surge of aircraft production, appreciable quantities of these materials are being used as stiffener for fabric-covered surfaces such as ailerns. However, nitrocellulose dopes are still more widely used for fabric han any other, and nitrocellulose lacquers are used on both the exterior nd the interior of metal planes.

In the early thirties, the United States dirigibles *Shenandoah* and *os Angeles* were said to comprise the major market for cellulose acetate oatings in the country. With the decline in this form of aerial navigation, nterest in this type of coating declined. It is interesting to note, however, hat the ill-fated dirigible *Hindenburg* is said to have been covered with abric protected with a highly esterified cellulose acetate butyrate, and one f the theories advanced to explain its destruction was that the large surace picked up a static charge which, when landing, sparked and set off the ydrogen with which its cells were filled.

The coating system used in applying today's aircraft fabric finishes comrises several brush coats of clear dope, followed by two similar coats pigmented with aluminum leaf or color to offer protection from sunlight. The ellulose esters are usually of D.P. about 250, and have 0.15 to 0.5 free ydroxyl groups per C_6 unit. Metal surfaces are finished with a primer nd two coats of lacquer.[79]

Analogous to fabric coatings are the flexible finishes used on leather and ubber. These require special formulations to provide the adhesion, exensibility, and toughness called for in such uses. The lacquer emulsions, nce thought to provide a way of reducing solvent costs so as to enable the acquer finishes to compete more readily with cheaper materials, have ound a place in leather finishing because they produce a coating which, vhile it has good adhesion, does not penetrate deeply into the leather, thus naintaining the original flexibility. Lacquer emulsions are particularly seful on garment and upholstery leathers. A lacquer emulsion is merely concentrated lacquer dope, made up with solvents higher boiling than vater and not miscible with it, dispersed, by the aid of a colloid mill, in vater containing a suitable emulsifying agent. On spraying or rollerpating the emulsion, the water penetrates into the porous surface or

[77] G. M. Kline and C. G. Malmberg, *Ind. Eng. Chem.*, **30**, 542 (1938).
[78] W. M. Billing (to Hercules Powder Co.), U. S. Patent 2,167,414 (July 25, 1939).
[79] M. Stiles, *Industrial Finishing*, **19**, No. 4, 38 (Feb., 1943).

evaporates, leaving the high-boiling solvent to join the "oil" droplets together and form the film.

A new development in the fabric-coating field is in progress with the availability of the heat-resisting cellulose esters and ethers. Based on their nonflammability, it comprises coating of hot (300°F.) viscous solutions of these materials in plasticizer directly on the fabric without use of solvent, and is directly related to the hot-melt coating of papers. As yet, these processes are used largely for waterproofing. Interlining for collars, cuffs, and apparel are also made by coating the liner cloth with a thermoplastic composition, and then adhering it in place with heat. Water resistance is the important property. Open-mesh fabrics and screens have been coated with plasticized cellulose acetate or mixed ester coatings for the last ten years, giving a product capable of transmitting the ultraviolet rays of the sun, this property being a characteristic of thin sections of these materials. While use of these materials has been restricted to portable solaria, hen houses, etc., where the therapeutic effect of the ultraviolet light is desired, in the last year such coated cloth, and a cheaper variant in which viscose solution is coated between the meshes, have come into use to replace bombed out windows.

(*c*) *Coated Paper*

During the last decade the use of papers coated with cellulose lacquers has become important. Applied to paper by roller coaters or like means, these lacquers serve a protective and decorative function. The wide development of cellophane wrapping became possible through the application of thin coatings of nitrocellulose lacquer to the transparent cellulose sheet, the lacquer containing a small amount of a wax, soluble in the solvent but incompatible with the coating material, which produced a film only several molecules thick atop the coating,[80] but reduced the permeability of the surface to water several hundredfold.

Papers may be coated to impart grease resistance and oil resistance, to improve washability of the surface, to protect foil adhered to paper, or for use in insulation. While the field was opened up with nitrocellulose lacquers, and the present uses of novelty and fancy papers are largely based on these finishes, the other cellulose derivatives are finding larger use in this

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[80] W. H. Charch and K. E. Prindle (to du Pont Cellophane Co.), U. S. Patents 1,737,187 (Nov. 26, 1930); 1,826,696 (Oct. 6, 1931); 1,826,699 (Oct. 6, 1931); W. H. Charch and N. A. Craigue (to du Pont Cellophane Co.), U. S. Patents 1,826,697-8 Oct. 6, 1931).

field; for instance, to resist cosmetic greases, etc., the acetate or mixed esters are being used more and more. One use which has been largely taken over by the ethyl ether of cellulose is in coating recording disks made of paper. This came about because of the need for a flame-resisting coating with a softness and cutting toughness which seems to be attainable only with this derivative. The water-soluble methyl ether of cellulose also finds some use as a greaseproofing agent for paper, and is of interest as a size in papermaking. A variety of cellulose derivatives are also used in making label lacquers both to improve appearance and to preserve the label.

(*d*) *Adhesives*

The use of the cellulose derivatives in adhesives again depends on a multiplicity of formulations for a multiplicity of specific uses. One of the largest is that described by Esselen[66] in sticking shoe soles to uppers with cements based on nitrocellulose, thereby eliminating much laborious sewing (61 million pairs[81] were so cemented in 1941). Thermoplastic adhesive strips for machine sealing of both paper- and cellophane-wrapped packages call for a number of varied combinations of cellulose derivatives, resins, and plasticizers. Household adhesives, useful for wood or ceramic repair, are largely nitrocellulose solutions in quick-drying solvents, often with aluminum powder or siliceous pigments dispersed in them to improve adhesion. Use of such adhesives in plywood or corrugated box manufacture has not been commercial because of cost; however, some interest has been shown in such materials to bind threads together to form ribbon, etc. A great many specialty adhesives are made from nitrocellulose and other cellulosic solutions; these include cements for the thermoplastic sealing of foil spots to the cork insert in bottle caps, adhesion of cotton floc to fabrics to give velvety effects, and impregnation of carpet backs to give added bond to piling fabrics; adhesives for making imitation felt lettering on cheap pennants, jerseys, etc.; and adhesives for temporary joints in electrical parts.

(*e*) *Varnish Bodying*

The use of the cellulose derivatives in varnish bodying and in raising the melting points of waxes has been a recent development largely restricted to ethylcellulose. In varnishes made with raw or blown oils and compatible resins, addition of ethylcellulose in amounts from 5 to 20% of the solids as a

[81] *The Du Pont Magazine*, **37**, No. 1, 8 (1943).

cold-cut or during runback[82] has been found to hasten drying time and to improve cold check resistance of the finish. Raising the melting points of waxes, important in times when normal natural waxes are high in price or scarce, is also an expanding field for use of ethylcellulose.

2. Films and Foils

The cellulose derivatives are the only materials which find use at present in providing supports for the flexible films used in photography. An industry of highly specialized and strict requirements, this use is based on the fact that the cellulose ester films, tough, flexible, and long-lasting, can be made in such highly purified forms that they have no deleterious effects on the sensitive photographic emulsions during their useful life. These materials are all sufficiently inert chemically to withstand the repeated immersion in developing and fixing fluids required, and are sufficiently long-lived to provide a lasting base for the developed photographic image. Of the cellulose esters used, nitrocellulose still makes up a large portion, finding a place chiefly in motion-picture film and roll or pack film for general use. Although the flammability of the nitrocellulose film presents some hazard if improperly handled, it finds general use in commercial motion-picture film of 33-mm. width because of its resistance to curling under high humidities, and its toughness which enables users to run the reels without breaking through the drive notches. This seems to depend largely on the hardness of the films, and nitrocellulose, giving the hardest films of any of the cellulose esters, is of real value here. The film compositions contain but little plasticizer, and that usually a solid, and the D.P. of the nitrocelluloses used in this field is generally about 250 to 300. The life of the average commercial motion-picture reel is about fifty projections, failure occurring through yellowing and cracking of the reel slots. This leaves a large amount of used film on hand, and a business has grown up of recovering the silver and nitrocellulose from the reels. The gelatin and emulsion are removed from the used film by digestion, and the purified film sold for use in textile coatings, etc.[83] In normal times several million pounds of this film scrap are used annually in the United States.

During recent years, the organic esters of cellulose have made inroads upon the place of nitrocellulose in photographic films, and have also extended their market considerably. In home motion pictures, where film

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[82] S. L. Bass and J. L. Sherk in J. J. Mattiello, *Protective and Decorative Coatings*. Vol. I, John Wiley, New York, 1941, p. 801.

[83] K. Bratring, *Nitrocellulose*, **4**, 161, 184 (1933).

6 mm. wide or smaller is used, the dimensional change due to film curling n exposure to humidity is less, and the size of the projected image is maller, so the distortion of the picture from this cause is of little practical ignificance. Also, the low flammability of the film base is a necessity for uch a household use. The longer life of the acetate film on storage (the J. S. Bureau of Standards has recently estimated that properly sealed eels of cellulose acetate film will last for centuries) has led to its widespread doption for the photographic duplication of commercial and government ecords, preservation of facsimiles of old documents, recording of detailed abulations of scientific results too bulky to publish, etc. In conjunction vith modern business machines, these systems provide very comprehensive ecords with but a fraction of the storage space required for the full-size ocuments. Where larger films which do not require projection are eeded and storage of the negatives is essential (x-ray film is an illustra-ion), cellulose acetate films are also used. These are based upon material f as high an acetylation as can be conveniently dissolved in film-casting olvents, to obtain as much water resistance as possible, and are of a D.P. round 300. In a transition period, such films were also based upon ellulose nitrate acetate.

In applications where resistance to distortion by humidity change must e of the highest order, the cellulose mixed esters find considerable use. or aerial mapping, photographing drawings and patterns for mass-produc-ion layouts, and x-ray films, the cellulose acetate butyrates and acetate ropionates, usually of a low degree of hydrolysis, find considerable market While their dimensional stability compares with that of the nitrocellulose ilms, they are somewhat softer, and this, combined with their higher costs nd relative scarcity of raw materials, has kept them from going into notion-picture films as yet. It is estimated that the amount of all cellulose sters used annually in photographic film in the United States is about 5 million pounds.

Under the heading of transparent film or foil are considered cellulose cetate and ethylcellulose sheeting now being produced and marketed for ses similar to cellophane. These materials are largely sold in sheets .00088 or 0.001 in. thick, and find use as insulating foil; as spacers in notor commutators and other electrical equipment when laminated to eavy paperboard; as protective lamination for menu cards, advertising ooklets, etc.; and in many packaging applications. Acetate foil is par-icularly favored in making windows for packages, because of its better vater resistance as compared with regenerated cellulose. It is estimated hat about 2.5 million pounds of cellulose acetate foil are sold annually in

the United States, all this material being of relatively thin nature and made by the casting process.

In this discussion of films and foils, particular reference is made to those films which are cast. Commercial methods of doing this involve the laying down of smooth, well-filtered solutions on a polished metal surface, such as nickel or chrome, or on a smooth gelatin surface laid on a polished copper base; conducting the wet cast film through a drying chamber with controlled atmosphere by means of this surface (large drum coaters and endless-band coaters being the usual types); peeling the partly dried film; further driving out solvent; and finally reeling. The metal surfaces may be either large drums or long polished endless metal belts. These operations are conducted under scrupulously clean conditions, especially during the making of photographic film, and solvent recovery is easily applied. By regulating the speed of the casting surface, or applying several coats, films as thick as 0.020 in. may be prepared. The photographic films are generally only slightly plasticized, but the wrapping materials may contain as much as 30% plasticizer. Ethylcellulose sheeting is largely made by the casting process, and is of particular interest in making shapes which can be drawn deeply from a flat sheet.

3. Plastics

The first synthetic plastic, celluloid, was made from a cellulose derivative, and the first large-scale industrial use of a chemical derivative of cellulose was in this plastic. There has been recently a rapid expansion in plastics and in the use of cellulose derivatives in plastics (Fig. 1[47]). The field of plastics can be most conveniently approached by considering the products in the chronological order of their development.

(*a*) *Celluloid*

Begun in the 1870's as a result of John Wesley Hyatt's efforts to produce a synthetic billiard ball, the manufacture of celluloid made the first cellulose plastic available. In the finished piece, celluloid is a relatively simple composition: cellulose nitrate of nitrogen content between 10.9 and 11.2%, compounded with camphor as the plasticizer, with requisite colors and stabilizing materials well mixed in.[84] The nitrocellulose used has a D.P.[85] of 500 to 600 and is found to form a rather tight complex with the

[84] J. W. Hyatt and I. S. Hyatt, U. S. Patent 105,338 (July 12, 1870).

[85] E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

mphor.[86] From the facts that the nitrocellulose used has one free ydroxyl group per C_6 unit, that a material of higher nitrogen content does ot work or bond in the process nearly so well, and that the composition of mplete complex formation, 35%, corresponds with that of a 1:1 mole tio of camphor to glucose units, it seems likely that this complex could be e result of hydrogen bonding between the oxygen in the camphor and the

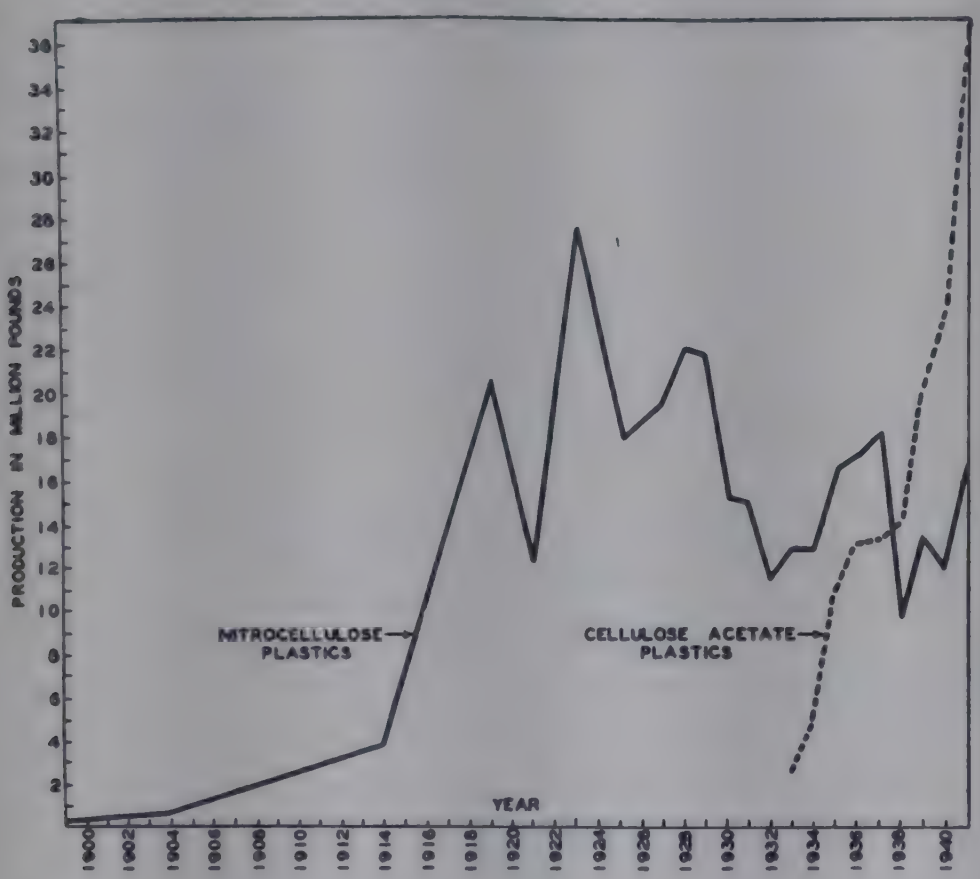

FIG. 1.—GROWTH OF NITROCELLULOSE AND CELLULOSE ACETATE PLASTICS INDUSTRY IN THE UNITED STATES (OTT[47]).
Based on U. S. Bureau of Census data.

ydroxyl of the cellulose nitrate. This arrangement would be expected to ow the distortion under heat and pressure, and resistance to cold flow nd water swelling so characteristic of celluloid,[47] since commercial cellu- ids contain only 26% camphor and thus allow for some cross-linking.

The process of making celluloid was first adapted from existing rubber achinery, and some of the types of equipment devised by Hyatt are in eneral use today. A flow sheet of the general operation is shown in igure 2. It is generally recognized that, save for its flammability, cellu- id has the best combination of physical properties of any of the thermo-

[86] J. C. Derksen, J. R. Katz, K. Hess, and C. Trogus, *Z. physik. Chem.*, A149, 371 930).

plastic materials available today. Its combination of hardness or rigidit and impact strength is not matched, and its dimensional stability unde

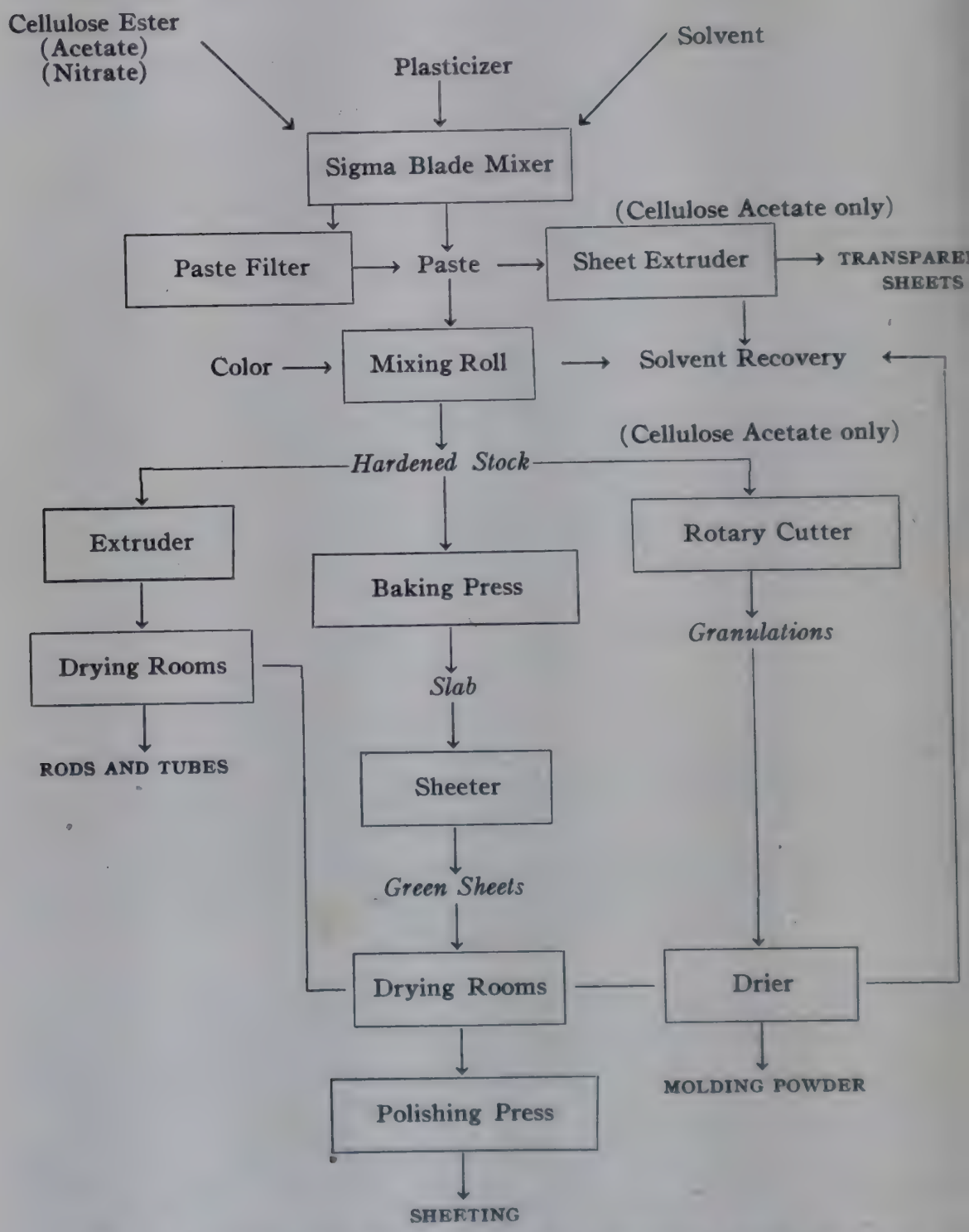

FIG. 2.—GENERALIZED FLOW SHEET FOR CELLULOSE ESTER PLASTICS

all conditions of use is very good. However, it is not generally rec mended for use at temperatures above 100°C. The process of manufac

is flexible, as shown by the flow diagram; sheets, rods, tubes, and molding blanks of all varieties are available in a profusion of colors, mottles, and novel effects.

In use, these standard shapes are usually pressed or blown, under heats up to 250°F., for periods of 10 to 15 min. and pressures up to 1500 lbs. per sq. in., into solid or hollow molded articles. For many articles, such as fountain pens, toiletware, and light novelties, celluloid is holding its own, but legislation against accumulation of quantities in stores of large cities, and the economies involved in injection molding, all tend to reduce its usage, as shown by Figure 1. The decrease in use of celluloid during 1930–1932 was largely caused by the adoption of cellulose acetate sheeting by the safety-glass industry as an interlayer, because of its superior resistance to ultraviolet light.[66] The rise in consumption after that time coincided with wider use in such volume articles as sheet coatings for "scuffproof" wooden heels, for umbrella handles, and for sanitary covers for toilet seats. Since 1939, consumption has been steady, more numerous miscellaneous uses compensating for the losses in some of the larger fields. In comparison with the rise in total consumption of cellulose plastics, celluloid has lost ground. War uses of celluloid plastics are many; fuse housings for trench mortar shells, powder containers, cartridge wads, and portable storage battery cases are among those recently developed.

It should be pointed out that the celluloid business depended in equal amount on the chemical availability of the raw materials and on advances in mechanical technique which made it possible to handle the plastic in production quantities. While the improvements in product and reduction in hazards in the trade have been the by-products of chemical research, it must nevertheless be pointed out that the best-known plasticizer for this material, despite the thousands of others suggested,[87] is still camphor.

(*b*) *Cellulose Acetate*

The evident failings of celluloid (flammability and yellowing under exposure to sunlight) were reasons for the exertion of a great deal of effort to find some other cellulose derivative that would overcome these objections without losing the good points of the cellulose nitrate plastic. After technicians had become familiar with the properties of cellulose acetate during the World War, a certain amount of material was made up by the block and sheet process in vogue with celluloid to provide nonflammable sheeting. The business did not grow rapidly; the plasticizers used were not always

[87] E. C. Worden, *Nitrocellulose Industry*. Van Nostrand, New York, 1921.

retained, the sheets and molded objects would warp badly and did not weather well, and they did not have the mechanical rigidity of celluloid sheeting. As a result, cellulose acetate did not find favor as a plastic material, despite considerable effort to find a suitable plasticizer for it. As the material is much less widely soluble than the nitrate ester, little real progress was made, although the use of molding granules based on cellulose acetate, which were molded in the same way and with the same equipment as was standard for the phenolic resins, did begin about 1928 with the commercialization of the toluenesulfonamide plasticizers.

However, it took another advance in mechanical technique to make the wide use of cellulose acetate plastics possible, and this time the methods of die casting, used in making small brass or zinc parts, were adapted to the injection molding of the cellulose acetate molding granules. This was first developed in Germany by Eichengrün during 1919 to 1924, small pieces being made by his *Spritzgussverfahren*. The injection molding process first came into wide industrial use in the United States in 1933. Legal restrictions on celluloid, reduction in price of cellulose acetate as a result of expanding acetate rayon manufacture, and need for a lower-cost molding process to compete with imported Japanese celluloid were the chief reasons for its coming into favor.

The development and progress of the technique of injection molding is well recorded in the literature[88, 89, 90]; because the process represents an advance in the handling of cellulosic materials, a short description of the method of molding will be given. Molding granules (Fig. 3[90]) are fed into the charge end of the heating cylinder as the injection plunger is withdrawn to its back position. The split cold mold is cleaned, closed, and brought into position in contact with the injection nozzle. The plunger moves forward, feeding cold stock into the heated chamber and displacing melted or plasticized material from around the spreader through the nozzle into the mold. The plunger is withdrawn, the mold kept closed for a few seconds to harden the molding so that it can be handled, the mold opened, the piece withdrawn, and the cycle repeated. Present-day machines handle from 1 to 16 oz. per shot, and operate on cycles from 5 sec. to 3 min. Pressures inside the cylinder are as high as 30,000 lbs. per sq. in., and temperatures as high as 500°F. The usual molding temperatures range from 350 to 400°F., the stock being heated for 5 to 12 min.

Advantages of the injection molding process include (a) high production

[88] Anon., *Chem.-Ztg.*, **42**, 409, 431 (1933).

[89] H. F. MacMillin, *Modern Plastics*, **14**, 249 (Oct., 1936).

[90] M. L. Macht, W. E. Rahm, and H. W. Paine, *Ind. Eng. Chem.*, **33**, 563 (1941).

rate due to fast cycles and constant temperatures of the heater and molds, (b) low mold cost since fewer cavities are required for a given production, (c) convenience in setting up the dies, (d) a low finishing cost after molding, due to elimination of fins at the parting line of the mold, (e) small material loss, since gates and sprues can be reground and reused, and (f) high thermal efficiency of the system. The limiting factor to the size of the injection seems to be the thin section of plastic needed to provide uniform heating of these poor heat conductors.[90] It is of interest to point out that, in this process, flow of the cellulose composition is made possible by lowering its viscosity by means of heat instead of solvent.

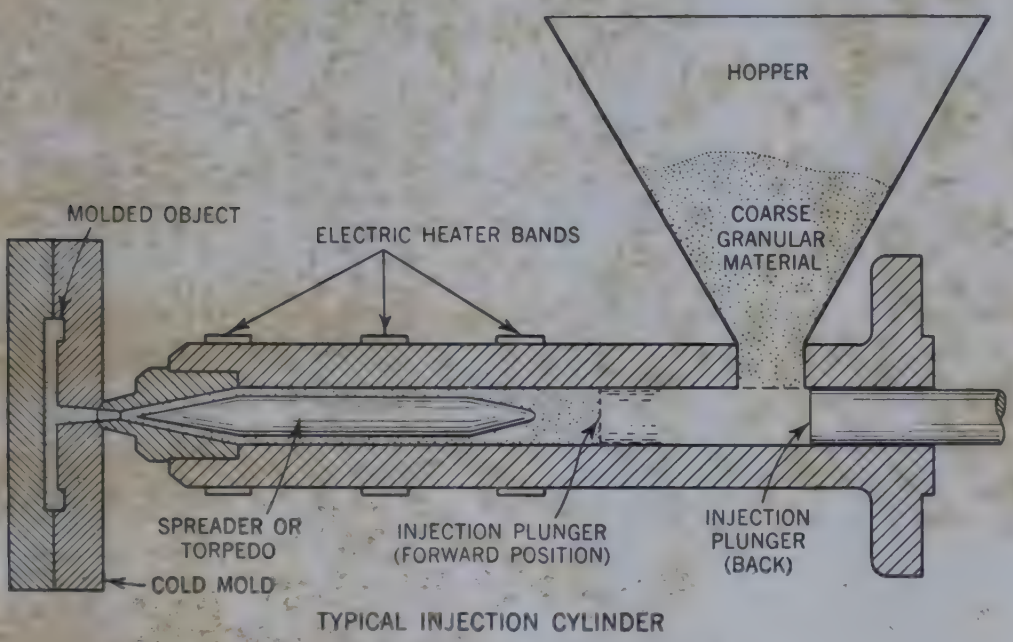

FIG. 3.—INJECTION MOLDING (MACHT, RAHM, AND PAINE[90]).

The molding powders used in this process are made either by a solvent process as outlined in Figure 2, or by a hot-rolling, nonsolvent process. The final plastic composition comprises both the cellulose acetate and plasticizing mixture, with only a few tenths per cent of volatile material. To get smooth injection, the molding powder granulations are usually dried for several hours to remove moisture just before molding.

As might be expected, the properties of the molding powder may be widely varied, depending on the cellulose acetate and plasticizers used. For molding, the optimum acetyl content of cellulose acetate ranges from 52 to 58% acetic acid content (0.8 to 0.35 free hydroxyl groups per C_6 unit). The lower acetyl materials give easier flow and somewhat better impact; the higher acetyl materials give more water-resistant plastics (Fig. 4[91])

[91] *Hercules Cellulose Acetate.* Hercules Powder Co., Wilmington, Del., 1941, p. 15.

and more resistance to humidity change. Cellulose acetate for injection molding usually has a D.P. of 300 or more. The effect of chain length on strength and deformation temperature of cellulose acetate plastics is

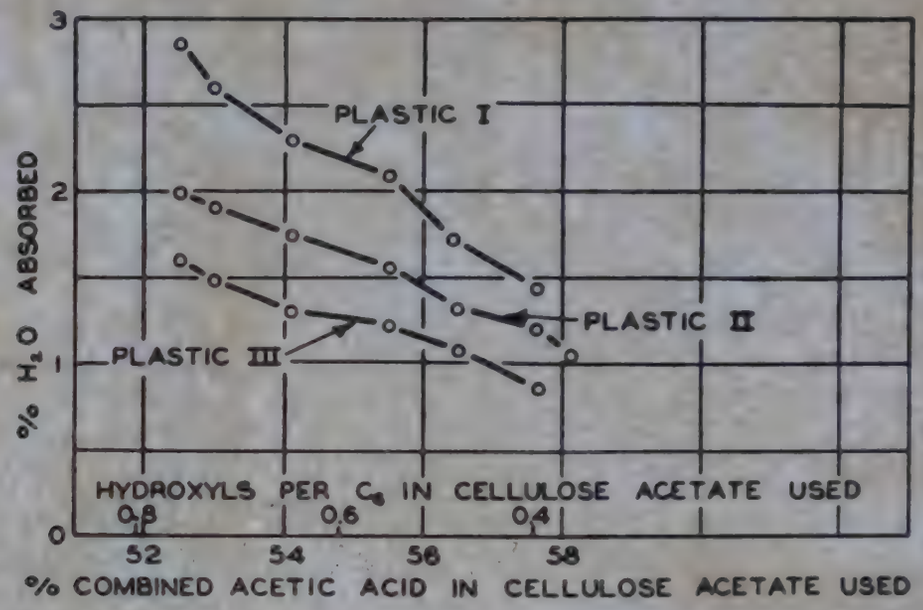

FIG. 4.—WATER ABSORPTION OF PLASTICS MADE FROM CELLULOSE ACETATE OF VARIED ACETYLATION (HERCULES POWDER COMPANY[91]).

Test disk (2-in. diameter and $^1/_4$-in. thick) immersed 96 hours in water at 69–71 °F.
Plastic I: 31% glycerol ester.
Plastic II: 31% alkyl phthalate.
Plastic III: 34% plasticizer, proportioned 2 alkyl phthalate, 2 phthalyl glycolate, 1 aryl phosphate.

illustrated (Table 10) by the following data on plastics made up with cellulose acetate of 53% acetic acid content, with viscosity (or chain length) varied as shown, and plasticized with 17% each of dimethyl and diethyl phthalates to 66 parts of cellulose acetate.

TABLE 10

EFFECT OF CHAIN LENGTH ON PROPERTIES OF CELLULOSE ACETATE PLASTICS

D.P. of cellulose acetate	Impact strength of plastic,[92] ft.-lbs./sq. in.	Flow temperature of plastic,[93] °C.
212	0.6	120
253	4.8	123.5
322	4.6	127
347	5.0	130
370	5.3	133

[92] Charpy impact test, A.S.T.M. *Standards 1941 Supplement*, D 256–41 T.
[93] A.S.T.M. *Standards 1941 Supplement*, D 569–41 T.

Despite the fact that no pains are taken to exclude air from the hot plastic in the injection cylinder, the loss in D.P. of the cellulose acetate in the molding powder is usually not greater than 10%, illustrating the purity and stability of the cellulose ester used in this application. The great change in impact strength found, as the D.P. of the cellulose acetate is increased above 212, indicates that in this ester, too, there is a chain length below which poor strength properties occur, and that to keep an acetate molding powder useful for several reinjections, the original ester must have a high enough viscosity to provide a factor of safety against embrittlement.

Growth of the use of cellulose plastics in the United States is illustrated by the data in Table 11.[94]

TABLE 11

USE OF CELLULOSE PLASTICS IN UNITED STATES, 1937–42[94]

Material	Thousands of pounds				
	1942[a]	1941	1940	1939	1937
Nitrocellulose sheets, rods, and tubes	15.128	16,497	11,800	13,357	18,122
Cellulose acetate sheets, rods, and tubes	7,453	6,384	8,887	9,141	18,923
Cellulose acetate molding powder	40,792[b]	30,716[b]	14,962	11,655	Combined in above

[a] Estimated for the whole year on the basis of U. S. Dept. of Commerce figures for the first 9 months of 1942.

[b] Includes molding powder based on cellulose acetate butyrate.

The other ingredient of the thermoplastic composition, the plasticizer, also determines the temperature required to make the composition flow as well as the final mechanical properties. In cellulose acetate, most true solvent plasticizers are acetic or propionic esters of alcohols and methyl or ethyl esters of acids of low volatility (b. p. 260°C. or higher), with the carbonyl groups arranged in linear or planar relationships in the molecule. These act as toughening in the finished plastic, while such ester groups attached to more complex molecular skeletons give brittle plastics.[95] For cellulose acetate there are no known plasticizers comparable to castor oil

[94] Compiled from U. S. Dept. of Commerce Reports.

[95] C. B. Gilbert and W. E. Gloor, *Ind. Eng. Chem.*, **33**, 597 (1941).

with nitrocellulose; while nonsolvents such as camphor or dibutyl phthal are used in cellulose acetate plastics, they tend to raise the temperat necessary for working. It appears that the action of acetate plasticizers the cellulose acetate may be largely accounted for by hydrogen bond between the carbonyl oxygen of the plasticizer and the free hydroxyl gr of the cellulose ester, since highly esterified celluloses do not respond v to thermoplastic molding processes. Systematic data on the effects plasticizers on various cellulose organic esters may be found in rec literature.[96, 97, 98] The plasticizers most commonly used with cellul acetate are the methyl and ethyl phthalates, triacetin and tripropionin, a methyl phthalylethyl glycolate as toughеners, and camphor, triphe phosphate, dibutyl phthalate, and dimethoxyethyl phthalate as modifi

In addition to many novelty uses, such as jewelry, household accessor dress decoration and buttons, goggles, combs and pencil barrels, and la articles such as handbag frames and umbrella handles, injection-mol cellulose acetate shapes find large usage in knobs, escutcheons and deco tive trim for automobiles, gas-mask parts, saw handles, pistol grips, fla light cases, telephone hand sets, adding machine housings, and such ap cations where weight, strength, color, and speed of production are imp tant. War uses for molded cellulose acetate plastics include gas-mask e pieces, Y-tubes, valves and valve guards, models of equipment for train spotters, aircraft lever knobs, inspection rings, light covers, interior tr speaking tubes, visors, bugles, utility boxes, radio parts, protecting cov for machinery in transit, thread-spacer shims, safety guards for machin and personnel, dimout screens, bullet tips, as well as several undisclo items of ordnance.

The introduction of the water-resisting higher-acetyl-content cellul acetate plastics has also put cellulose acetate into direct competition w nitrocellulose as a material for making toothbrush handles and fountain p barrels. Cellulose acetate sheeting finds use in aircraft transparenc particularly in slower aircraft; as shatterproof windows, either alone or inforced with wire; in watch crystals and clock faces; and in transparent spection ports of all kinds, on both aircraft and machinery. Clear tra parencies for gliders are being made entirely of cellulose acetate, and t plastic appears to offer more protection against sunburn to high-altitu

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[96] A. Kirkpatrick, *J. Applied Phys.*, **11**, 255 (1940); W. E. Gloor, *J. App Phys.*, **12**, 420 (1941).

[97] R. Houwink, *Elasticity, Plasticity, and Structure of Matter*. Univ. Press, C bridge, 1937, p. 243.

[98] C. R. Fordyce and L. W. A. Meyer, *Ind. Eng. Chem.*, **32**, 1053 (1940).

rs than the acrylic resins. Other wartime uses for cellulose acetate eting include shatter-resistant windows for barracks and blimps, motor-le wind shields, bomber turrets, antenna housings, windows for gas-tective boxes, and dust guards. It is also used as a supporting mem-ne for polarizing crystals in glare-resisting goggle lenses for pilots and k drivers. At one time it was the sole material used in making nondis-oring safety-glass interlayer for automobile use,[90] being turned out in ets of 0.025 in. thickness in rolls 50 in. wide and thousands of feet long. wever, the special machinery developed for this purpose proved capable handling vinyl resins such as the butyral just as easily, and, since these ve a tougher lamination at low temperatures and such good adhesion to ss that no sealing compounds were required, they are now used in at least % of the safety glass made in the United States.

A newly initiated but promising application of cellulose acetate sheeting the use of films 5 to 20 mils in thickness for use as a package for display rchandise. Attractive square or cylindrical boxes are made from sheet-, either by the block and sheet method or continuous sheet process de-oped for safety-glass interlayer, and used for display boxes for items nging from thread and cake to orchids. With emphasis being laid on eye peal to sell merchandise, these light, tough containers have been found to pply this selling stimulus. When business conditions develop another yer's market, it is expected that the use of these transparencies will more an make up for the loss of the safety-glass market to cellulose acetate eeting.

(*c*) *Cellulose Mixed Esters*

While the probable limits to the consumption of the cellulose ester plas-s have not yet been visualized, certain defects have been found in the llulose acetate materials which do not permit their use in applications hich require great adherence to dimension over long periods of time, sistance to heat and humidity, and weathering or exposure to tropical sea . The development of the higher-acetic acid-content molding com-unds was a partial answer to this objection, but, concurrently, molding wders based on cellulose acetate butyrate made their appearance. hese materials, despite a propensity to emit odor during molding, find uch use especially in the making of larger injection moldings, where their ater resistance and small content of nonvolatile plasticizer, such as the tyl or amyl phthalates, combine to largely eliminate warping of the

[90] G. B. Watkins and J. D. Ryan, *Ind. Eng. Chem.*, **25**, 1192 (1933).

plastic. In 1941 it is estimated that about 2 million pounds of high-acetyl molding powder, and 6 million pounds of mixed ester material, were used in the United States.

The cellulose acetate butyrate used is generally a material of about 14% acetyl content and 36% butyryl content or, in terms of substitution, 1.1 acetyl, 1.6 butyryl, and 0.3 hydroxyl groups per C_6 unit. These esters are described as more soluble in ester and hydrocarbon solvents than cellulose acetate[69] and, hence, are completely miscible with the higher-ester plasticizers. The large content of butyryl also makes them somewhat more "self-plasticized" by virtue of greater weight of noncellulosic substituent and, hence, they require less plasticizer to produce a given hardness, and give smooth injection, perhaps as a result of the lubrication of the chains past each other as suggested by Houwink.[100] In general, chain length of these mixed esters ranges between D.P. 250 and 350, production of higher-viscosity types being difficult. Due to low water absorption and volatile content, their weather resistance is quite good. This material is also not likely to lose plasticizer to nitrocellulose lacquer films, as has been noticed with some cellulose acetate plastics in contact with lacquer, probably because the plasticizers are less active solvents for the nitrocellulose and have no reason to migrate. Uses for mixed ester plastics include large automobile panels, outside ornaments and name plates, gun stocks, ordnance parts such as ammunition rollers, pistol grips and bayonet scabbards, colored strands for outdoor furniture, radio and office machine housings, as well as novelty work.

It is believed that the future of the cellulose plastics, in the competitive state that is bound to arise with the introduction and cheapening of the various thermoplastic synthetic resins such as copolymer vinyl chloride-acetate, polystyrene, polyacrylates of various kinds, and possible polyethylenes, lies in the higher acetyl acetates, mixed esters, and ethylcellulose plastics. Under present conditions, it seems that the acetate plastics will always be cheaper to make than the esters based on higher fatty acids.

(*d*) *Ethylcellulose*

Called the cellulose derivative of the future for protective coatings, ethylcellulose already has aroused lively interest and finds some sale in the plastics markets. Of interest because of its low-temperature flexibility, combined with low flammability, water and light resistance, dimensional stability, and freedom from potential odor, the lack of oil resistance of the

[100] R. Houwink, *Elasticity, Plasticity, and Structure of Matter*, p. 245; see ref. 97, p. 1098.

47 to 48% ethoxyl grades offered for protective coatings seemed a formidable handicap, coupled with the serious lamination that was encountered when plastics based on this material were injection molded. However, use of ethylations around 45% ethoxyl gave acceptable oil resistance, and proper choice of plasticizers led to a set of plastics which seem practical and found use to the extent of at least 250,000 lbs. in 1941 and over one million pounds in 1942, in the United States. The oil and cold resistance of ethylcellulose, coupled with the good electrical properties of the material, make it of particular value in the production of insulating tubing, etc. This is extruded by a variation of the rubber extruder adapted to high-temperature use,[101] and it appears that all thermoplastic cellulose derivatives will find increased usage because of the development of this new technique. While cellulose acetate and mixed ester plastics are being formed in quantity in standard shapes to replace aluminum and other metals temporarily not available because of war need, in applications such as table trimming, wall-panel jointing, and decorative automobile trim, the newly developed ethylcellulose plastics are also being coated on wire at rates as high as 500 ft. a minute by the hot extrusion technique. Dress belts of toughness comparable with that of vinyl plastics, as well as the standard trim shapes, are being extruded with ethylcellulose plastics; and, in the injection field, large moldings such as radio cabinets and housings, as well as sanitary accessories such as toothbrush handles, are being molded of the material. War time uses of ethylcellulose reflect largely its superior low-temperature resistance in such things as lamp housings of all sizes, control knobs, radio parts, and water containers. The ability to fashion soft rubberlike plastics from available oils and ethylcellulose has given rise to a number of military applications of these materials, including grommets, door cushions, drain tubes, roof and window sealing strips, and container gaskets. The material seems fully competitive with mixed ester plastics in dimensional stability under humidity or temperature change, is the best thing available for low-temperature resistance, but does not lend itself as yet to a full range of colors, including crystal.

Since ethylcellulose is a new material, and especially since it exemplifies a new chemical type, it is to be expected that it will have to undergo a long period of improvement of both product and process to meet the standards of the plastic users as regards color and other properties. It took 100 years, from Braconnot's discovery of nitrated cellulose in 1833 until 1930, to make a nitrocellulose that would give a good crystal tint; it took

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[101] P. C. Goodspeed, *Modern Plastics*, **18**, 35 (July, 1941).

TABLE 12

COMPARISON OF PROPERTIES OF COMMERCIAL PLASTICS

(Data from *Modern Plastics Catalog*, 1941; Hercules Powder Company Laboratory; and manufacturers' publications)

Property	Celluloid (Pyralin, Fiberloid, Xylonite, etc.)	Cellulose acetate (Tenite, Fibestos, Trolit, Lumarith, Plastacele, etc.)	Ethyl cellulose (Ethocel, Lumarith EC, etc.)	Cellulose acetate butyrate (Tenite II)	Polystyrene (Lustron, Loalin, etc.)	Methyl methacrylate (Lucite, Crystalite, etc.)	Phenol-formaldehyde, asbestos-filled
Specific gravity	1.4	1.3	1.13	1.2	1.05	1.19	1.3
Stability toward:							
Acids	Good	Poor	Poor	Poor	Resistant	..	Resistant
Bases	Poor	Poor	Good	Fair	Resistant	..	Poor
Water, % absorption[a]	0.5–1.0	1.1–3.0	0.4–1.1	0.7–1.2	0.05	0.20	0.20
Weathering	Fair, discolors	Poor	Fair to poor	Good	Very poor	Good	Fair, discolors
Best color obtainable	Nearly water-white	Nearly water-white	Light amber	Most crystal shades	Water-white	Water-white	Darker shades
Impact strength[b]	1.5–2.5	0.8–3.2	1.2–5.0	0.4–4.5	0.35–0.50	0.2–0.5	0.2–0.7
Tensile strength, lbs./sq. in.	5000–10,000	5000–10,000	6000–9000	2500–7500	5000–9000	4000–9000	4000–10,000
% Elongation	10–40	15–50	10–40	8–80	2–5	1–15	....
Modulus of elasticity, lbs./sq. in. $\times 10^5$	2–4	1–3.5	1–5	2–3.5	1.7–2.0	4–6	10–45
Rockwell hardness[c]	25 to 50	−25 to 75	−25 to 80	0 to 80	80 to 90	70	85 to 120
Useful temperature range, °F. (upper limit)	160	140–220	140–180	140–250	140–170	120–160	450
Flow temperature range, °F.[d]	290–305	240–340	212–305	240–320	260	266–275	..

Volume resistivity, ohm/cm. at 50% R.H., 25°C.	10^{10}	10^{12}	10^{15}	10^{12}	10^{13}	10^{15}	10^{16}
Dielectric constant, 1000 cycles, 25°C.		3.5–7	2.5–3.5	3.5–6	2.5–2.6	3.3	4.5–20
Power factor, 1000 cycles, 25°C.		0.01–0.06	0.005–0.025	0.01–0.06	0.0001	0.06–0.07	0.1–0.05
Dielectric strength, volts/mil	600–1200	350–1000	1500	400	500–700	500	400
Thermal conductivity $\times 10^{-4}$, cal./sec./sq. cm./°C./cm.	3.1–5.1	4.5–7.8	5.6	4.5–7.8	2	1–10	8–20
Specific heat	0.33–0.38	0.37–0.42	0.32–0.46	0.41	0.32	0.35	0.30
Thermal expansion, increase/ unit length $\times 10^{-5}$/°C.	12–16	8–16	10–14	11–16	7	8–9	2.5–4

[a] Method of A.S.T.M. Standard D 570–40 T, using a disk 2 in. in diameter by 1/4 in. thick, 96-hr. immersion.

[b] Expressed as energy to break, ft.-lbs. per in. of notch, Charpy bar, by A.S.T.M. Standard, D 256–38.

[c] Hardness Rockwell M scale at 70°F. and 50% relative humidity, by A.S.T.M. Standard, D 229–39.

[d] Flow temperature in °F. by A.S.T.M. Standard, D 569–40 T.

from 1905 to 1937 to produce a crystal cellulose acetate; the mixed esters patented in 1929 are still being improved with regard to color, so it appears that the producers of ethylcellulose should, after a decade or so of effort, be able to meet this requirement also.

(e) *Other Cellulose Derivatives*

While some small use of cellulose acetate propionate has been reported in sheet stock and lacquer, none of the other cellulose derivatives, such as propionate, acetate stearate, methyl ether, hydroxyethyl ether, and glycolic ether, have found any commercial use in plastics. Benzylcellulose at one time found a limited market in dentures. Properties of the cellulose plastics with three of their synthetic competitors are shown in Table 12.

4. Explosives

In explosives, the only derivative of use is the nitrate ester. The use may be divided in two parts: (a) as a stiffening agent for blasting gelatins, and (b) as the major ingredient in propellent powders whether single- or double-base.

The nitrocellulose used in blasting gelatin is, according to Kraemer,[85] of the greatest D.P. (about 3000–3500) of any of the commercial cellulose derivatives. This is not surprising when it is considered that the cellulose used has had but mild purification, and that the use of the nitrocellulose is merely to hold the nitroglycerin in a less shock-sensitive form, yet provide a powerful shattering blast. Blasting gelatins are composed of about 9 parts of nitroglycerin to one part of dynamite nitrocellulose, and are produced by mixing the two ingredients in a two-shaft mixer. The material is packed in sticks, and finds its greatest use in wet work, where its high water resistance permits loading under water, and in rock blasting, particularly tunneling where the sharp blast shatters the rock into small pieces which are easily removed. It is of interest to note that the gel obtained as a result of the colloiding of the nitrocellulose by the nitroglycerin is sufficient to eliminate entirely the extreme care necessary to avoid sudden shocks which makes the handling of nitroglycerin liquid so treacherous. The nitrocellulose used for this purpose, of about 12.3% nitrogen content, contributes to the blast upon detonation. Gelatin dynamites contain sodium nitrate, charcoal, sulfur, and carbonaceous materials, mixed in with the colloid in the lower grades.

The propellent uses of nitrocellulose are based upon the discoveries of Schönbein and Abel, in the middle of the last century, that this material would give a powerful smokeless explosive, and that to be used it had to be

roperly stabilized and granulated. The first efforts to use nitrocellulose n explosives were made in Austria, but the products, of fibrous texture, ould not be properly stabilized and were apt to burn too fast and burst the uns. The work of Abel, in stabilizing the product, led to its use in blasting xplosives, which was its major use for many years. Compressed wet high-rade nitrocellulose (13.4% N) was used for years as the explosive charge in Whitehead torpedos. The first practical smokeless powder was made by he French chemist P. Vielle, who colloided nitrocellulose of 13% nitration vith ether-alcohol mixture, and rolled the paste into thin sheets, cut the heets into squares, and dried them. This early gunpowder procedure is uite like thermoplastic molding powder procedures described under plas-ics. These colloided grains had sufficiently slow-burning properties to nake them of value in ballistic work, and they were followed by the de-elopment of double-base powders (nitrocellulose gelatinized together with itroglycerin as in ballistite or cordite) and the flashless nonhygroscopic mokeless powders. Most all modern powders are colloided with alcohol nd ether or alcohol and acetone, formed into grains of suitable size, and hen treated to remove the volatile solvent.

Double-base powders are still made extensively for use in sporting rifle nd shotgun cartridges and are also used for particular military uses vhere it is desirable to take advantage of the characteristics of these pow-lers. Double-base powders are made using from 5 to 40% of nitroglycerin vith nitrocellulose together with inorganic salts to control flash and with liphenylamine as a stabilizer. These powders have the following advan-tages: They are almost entirely nonhygroscopic and thus are less affected by humidity at time of loading; are much more ballistically stable; and also possess a higher potential, making them useful in cases where maximum performance is required, as in high-velocity guns. Double-base powders are nore easily ignited than single-base powders and are more uniform burning.

The flow sheet[102] (Fig. 5) indicates the process now used in making single-base smokeless powders. Formulas[103] used today are represented by:

Nitrocellulose (13.15% blend)	85%	76%
Dinitrotoluene	10%	23%
Dibutyl Phthalate	5%	..
Diphenylamine	1%*	1%

* Added.

[102] *Military Explosives.* War Dept., Tech. Manual No. 9-2900, Washington, Aug. 29, 1940, p. 7.

[103] R. G. Woodbridge (to du Pont Co.), U. S. Patent 1,854,776 (Apr. 19, 1932); E. S. Goodyear (to Hercules Powder Co.), U. S. Patent 2,228,309 (Jan. 14, 1941).

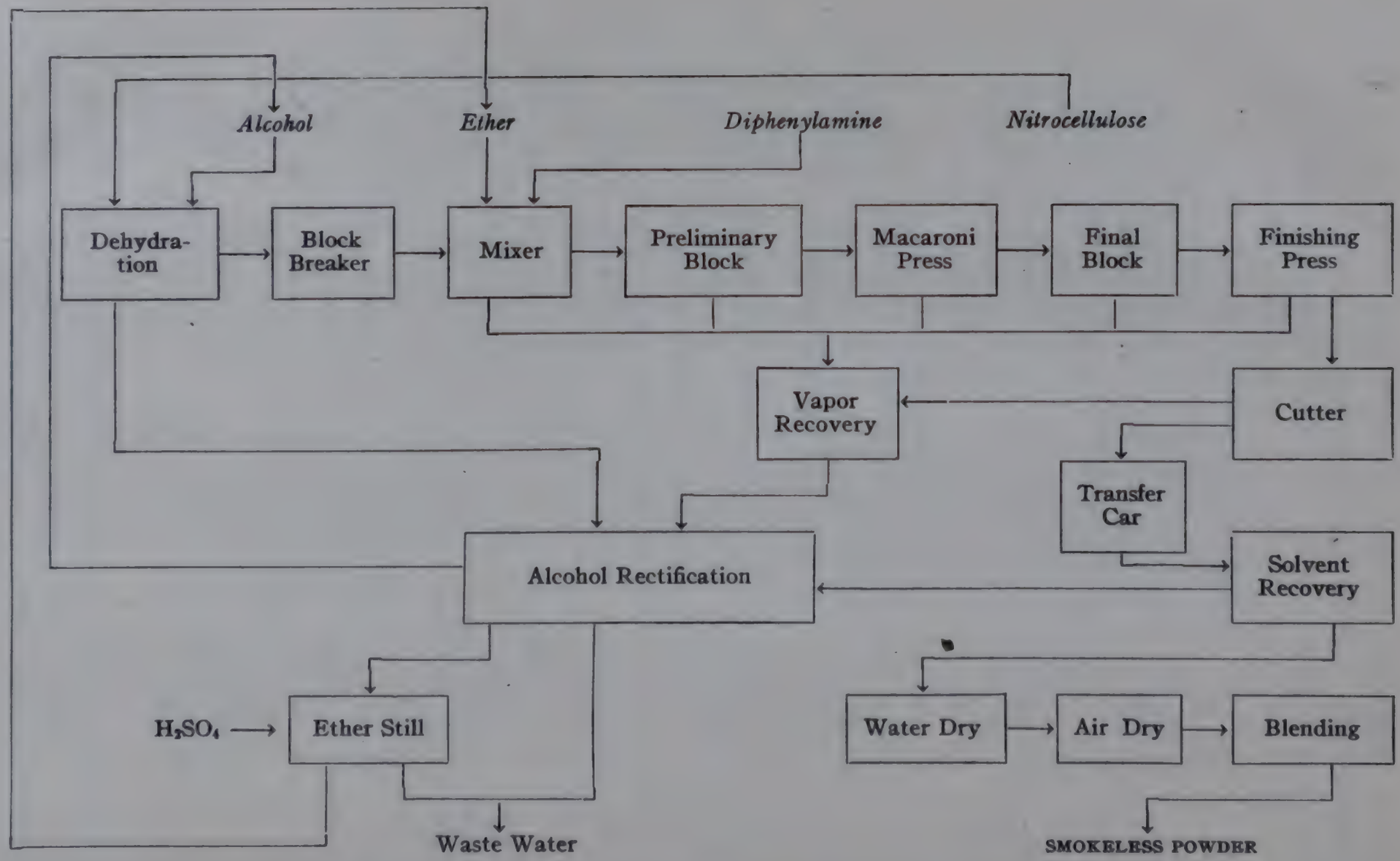

FIG. 5.—FLOW SHEET FOR SINGLE-BASE SMOKELESS POWDER PREPARATION.[102]

Practically all modern powders are made from a blend of 12.6 and 13.33% nitrogen content to give a nitrogen content of 12.75% or more. Diphenylamine is used in the formula as a stabilizer, reacting with nitrogen oxides formed by decomposition of the nitrocellulose to keep the material free of acidity on storage, since decomposition becomes autocatalytic if the acid products are allowed to remain in contact with the nitrocellulose. This amine and the diphenylnitrosamine first formed with nitric acid are stabilizers, and perhaps the more highly nitrated derivatives also help reduce the acidity. The dinitrotoluene is used as a retarder to get slower burning; it also has a cooling action and reduces flash. It is stated that one pound of nitrocellulose of 12.60% nitrogen content when burned liberates 1,425,000 ft.-lbs. of energy. Addition of the inert ingredients reduces the energy liberated per pound of explosive by the combustion and also retards the rate of burning. In modern small arms powder, burning rate is also controlled by coating the surface with a moderant such as dinitrotoluene, ethyl Centralite, or other plasticizer. Production in peacetime of these smokeless powders is restricted largely to material for sporting and hunting use; in time of war, enormous quantities of these materials are produced. Where a peacetime production of perhaps 5 million pounds of powder suffices annually for the United States, the facilities for making military explosives have been so widely expanded in the United States that smokeless powder production is running well ahead of other armament output in 1942.

From the standpoint of the colloid chemistry of cellulose derivatives, the production of smokeless powder from cellulose nitrate involves a change in density and orientation of the ester which makes a denser, hence slower-burning, material. It is perhaps not generally recognized that the smokeless powders are not homogeneous colloids; that, while solvent and plasticizer may be incorporated in the material during the process of converting the fibrous, comminuted nitrocellulose fibers into strands, probably half the nitrocellulose retains its fibrous structure, being more or less cemented in place by the remaining colloided material. In fact, this structure is often sought by making a blend of the material containing 12.60 and 13.2% nitrogen in preparing the mix. The lower-nitrogen-content constituent, being more soluble in the ether-alcohol mixes used, largely forms the cementing colloid. While chain length of these materials is of the order of D.P. 500, the tough nature of the colloided grains assists in keeping a uniform burning powder, since a friable material, on being exposed to the shock of an igniter charge, would shatter and develop excessive pressures due to such rapid combustion that it would rupture the gun barrel.

Variations in the formulation of smokeless powders are made, such as addition of inorganic nitrates to the colloid to reduce the flash of the gun, and addition of graphite and similar materials to retard burning and provide protection against moisture absorption, but in all these the principal explosive ingredient is the nitrocellulose.

5. Miscellaneous Uses

While there are a great many miscellaneous uses of the cellulose derivatives, some of which amount to very little from the strictly commercial point of view, yet a number of these are of interest and merit some mention.

In the field of cosmetics, for instance, nitrocellulose solutions of various kinds form the base of most of the nail polishes sold. Cellulose acetate solutions have been sold as cements to stop runs in women's hosiery. Ethylcellulose finds some place as an ingredient in lipstick waxes, and methylcellulose sols in water form the basis of hair wave-set fluids. Cellulose mixed ester films are used as coatings on jar lids to resist the action of cosmetic creams.

Included in this category are the uses of the cellulose derivatives in printing inks, where heavily pigmented solutions in high-boiling solvents (180 to 220°C.) find application. Low-viscosity ethylcellulose and cellulose nitrate find principal use here, the latter in largest volume. In rotogravure printing, nitrocellulose inks are used because of the high speeds made possible by the rapid solvent release of nitrocellulose. For special chemical resistance, ethylcellulose finds use in inks. The impregnation of felts for the manufacture of box toes for the inside of shoes uses considerable amounts of cellulose derivatives. Sodium cellulose glycolate and ethylcellulose emulsions find some use as dye leveling agents.

In countries where a large supply of starch is not available, methylcellulose has found some use as a replacement for starch in such things as wallpaper paste. In Germany it is reported that for these purposes, a 2% solution of methylcellulose is taking the place of a 40% starch paste, at an equal material cost.

D. FUTURE APPLICATIONS

While the record of accomplishment in applying cellulose derivatives is varied and large, it will be seen that the thread of pioneering runs through most of the uses described, and that efforts are continually being made to provide improved derivatives which will overcome small defects of those first used.

From the technical standpoint, it is probable that more can be obtained

from our existing materials through better handling methods. In Houwink's book[97] the contrast between physical properties of oriented and non-oriented cellulose derivatives is emphasized by devoting a section of the chapter on cellulose to each type of material. Methods of orienting cellulose plastics, for instance, may be developed to improve the strength of existing compounds. Working of cellulosic materials at temperatures at which they are in the high elasticity region, that is, 10^5 to 10^7 poises, will probably also be developed as a means of improving properties of cellulosic materials. Application of knowledge concerning strengths of cellulose as it relates to the amount of crystal structure present should also lead to improvement in the present products. Development of cellulose plastics to a stage in which they will be thermosetting is hinted at by recent work of Garvey[104]; such a course would combine the good physical properties of the heat-hardening materials with the ease of fabrication characteristic of thermoplastics.

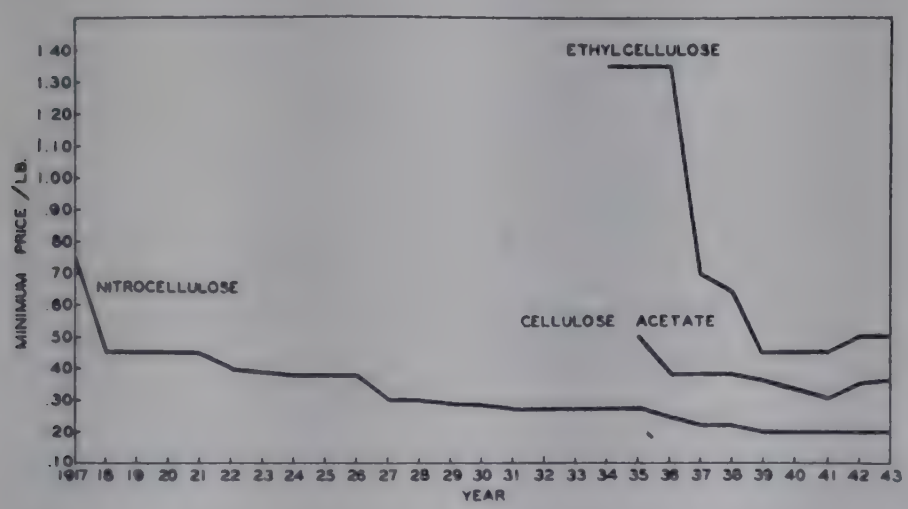

FIG. 6.—PRICE TRENDS FOR CELLULOSE DERIVATIVES (OTT[47]).

From the commercial standpoint, the cellulose derivative industries offer a record of price reduction as illustrated in Figure 6.[47] The cellulose derivatives appear to be in a good competitive position because of the prospect of (1) cheaper solvents, acids, and anhydrides for esterification, and (2) the naturally polymerized cellulose becoming economically available from various sources as proper processing procedures are developed. Since it seems possible that future development of agricultural products as sources of chemical raw materials will be extensive, it is certainly within

[104] B. S. Garvey, C. H. Alexander, F. E. Küng, and D. E. Henderson, *Ind. Eng. Chem.*, **33**, 1060 (1941).

reason to expect expansion of these cellulose materials in the lacquer and plastic fields, with the cellulose, esterifying or etherifying groups, plasticizers, and solvents all attained from annual crops. Such a widespread development would for the first time give civilization the hope of a perpetual supply of raw materials based on annually renewed sources rather than on exhaustible mineral resources, and would do much to remove the causes of international conflict.

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